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SOLID ROCKET PROPELLANTS

by

Krzysztof Krowicki and Michal Syczewski



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By: Krzysztof Krowicki and Michal Syczewski

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ABSTRACT: This book is intended for scientific workers interested in combustion problems, for students of higher and middle technical schools, and for technicians. It should be useful to a wide circle of rocket modelers. The book gives basic theoretical information on such physicochemical properties of solid rocket fuels as burning mechanism, thrust, combustion, and ignition. It also gives information on chemical problems connected with solid fuels and cites numerous examples of specific fuels. The authors sincerely thank Professor Doctor Dionizy Smolenski for exceptionally valuable remarks and suggestions which made it possible to avoid a number of errors and mistakes. They thank also Doctor Engineer Zygmunt Bonecki who gave the initiative for writing the book. Special recognition is expressed to Zofia Sosnowska for her keen and expert editing. This book is the first Polish publication dedicated exclusively to solid rocket fuels. English Translation: 350 pages.

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#### FROM THE AUTHORS

More and more specialists are concerning themselves with rocket propulsion technology. This is an area of interest not only for military experts but also for specialists in the fields of meteorology, communication and air transportation and for a multitude of rocketry amateurs congregated into various organizations, principally IOK.

Domestic literature is currently lacking in comprehensive publications on the subject of the chemistry and technology of solid rocket propellants. Nor are the publications encountered in the world literature very exhaustive. The reasons for this are the widely divergent compositions of present-day solid rocket propellants and the fact that much data in this field are bound up in military and industrial secrecy. Nevertheless, certain bits of information on this subject do occasionally find their way into publications.

This work is precisely for the purpose of treating this material. It is an attempt to assemble and systematize the most interesting and important information appearing in monograph publications, reports and patents. The assembled material is of the greatest value for specialists engaged in scientific research work in the discipline of solid rocket propellants, technicians and students. The accessibility of the material offered in this book also makes it invaluable to rocketry enthusiasts.

The various portions of the book were written by the following authors: Part I, Mgr. Eng. Michal Syczewski, except for Chapters 1, 1.1, 1.2, 1.3, 4, 4.1, 4.2 and 4.3, which were written by Mgr. Krzysztof Krowicki, who also wrote Parts II and III.

Delivering this book into the hands of its readers, we hope that it will inspire increased research on solid rocket propellants in our land.

We wish to thank Prof. Dr. Dioniz Smolenski for his extraordinarily valuable counsel which enabled us to avoid many errors and inaccuracies. We also wish to express our gratitude to Zygmunt Bonecki, upon whose initiative this book was written. We extend special recognition to editor Zofia Sosnowski for her able and perceptive work in composing this book.

## LIST OF THE MORE IMPORTANT SYMBOLS AND ABBREVIATIONS

### Latin Symbols

- A = thermal equivalent of work
- A = cross section
- A<sub>sp</sub> = combustion area of the charge
- A<sub>ad</sub> = work of adhesion
- A<sub>coh</sub> = work of cohesion
- A<sub>p</sub> = cross-sectional area through the channel of free flow
- A<sub>cr</sub> = critical cross-sectional area of the nozzle
- A<sub>po</sub> = cross-sectional area of the grain
- A<sub>o</sub> = cross-sectional area of the chamber
- a = acceleration
- a = coefficient in combustion law
- a = the speed of sound
- a = activity
- a<sub>p</sub> = total elongation
- B = constant in non-Newtonian flow equation
- C<sub>o</sub> = fuel consumption coefficient
- C<sub>v</sub> = molar specific heat of gas at a constant volume
- C<sub>p</sub> = molar specific heat of gas at constant pressure
- C = constant in equation for erosive combustion
- c = concentration
- c<sub>v</sub> = specific heat at constant volume
- c<sub>p</sub> = specific heat at constant pressure
- c<sub>sp</sub> = specific heat of solid propellant
- c = constriction during elongation
- d = diameter



$D$  = diameter  
 $D$  = rate of flow  
 $E$  = activation energy  
 $E$  = elasticity modulus (a constant for a given material)  
 $F$  = thrust  
 $G$  = mass fuel consumption (mass output)  
 $g$  = acceleration of gravity  
 $H^\circ$  = molal enthalpy  
 $h$  = thickness of chamber walls  
 $I$  = number of chemically bound atoms of an element  
 $I$  = total impulse  
 $I_s = I_{w1}$  = individual or specific impulse  
 $I_{sob}$  = unit volume impulse (specific density impulse)  
 $i$  = number of gram atoms of an element in 1 kg of propellant component  
 $i_e$  = total enthalpy  
 $J$  = ratio of cross-sectional area through the channel of free flow to the critical cross-sectional area of the nozzle  
 $j$  = longitudinal rocket acceleration  
 $K$  = constant in erosion equation  
 $K_{wg}$  = water gas equilibrium constant  
 $K_I$  = internal contraction constant  
 $K_n$  = contraction constant  
 $K_N$  = cost of 1 kg of rocket construction  
 $K_p$  = cost of 1 kg of propellant  
 $k$  = adiabatic exponent  
 $k_r$  = permissible stretching tension (stress)  
 $L$  = length  
 $L$  = work expended in breaking samples by drop-testing  
 $l$  = length

$M$	= molecular weight
$M$	= Mach number
$m$	= wave number of tangential waves
$m$	= gas mass
$m$	= mass velocity in erosivity equation
$m^*$	= mass velocity when $M = 1$
$n$	= power exponent in combustion law
$n$	= wave number of radiation waves
$n$	= power exponent for non-Newtonian flow
$n_D$	= coefficient of light refraction
$Pr$	= Prandtl number
$P$	= pressure
$Q$	= mass velocity of diffusing gas in a combustion equation
$q$	= wave number of axial vibrations
$q$	= surface area of liquid
$Q_r$	= plasticity limit
$Re$	= Reynolds number
$R$	= gas constant
$R$	= radius
$R_{el}$	= elasticity limit
$R_r$	= tensile strength
$r$	= burning rate
$r_e$	= erosive burning rate
$r_p$	= burning rate without erosion
$S$	= diffusion coefficient
$T$	= absolute gas temperature
$T_f$	= flame temperature
$T_s$	= surface temperature of the burning propellant
$T_i$	= initial propellant temperature

$T_p$  = temperature of isobaric primer combustion  
 $t$  = duration time of acceleration  
 $U$  = impact strength  
 $U$  = rate of fall of a solid body in a liquid  
 $U$  = linear gas flow rate as defined by Reynolds numbers  
 $u$  = temperature coefficient of burning rate  
 $V$  = volume  
 $v$  = rate of flowing gases in erosion studies  
 $W_1$  = final velocity of expelled gases  
 $W_0$  = initial gas velocity  
 $W_p$  = weight of the propellant  
 $W_R$  = starting weight of entire rocket without payload  
 $W_z$  = mass of primer  
 $z$  = summary power exponent in erosive combustion laws

#### Greek symbols

$\alpha$  = summary constant in erosive combustion equation  
 $\alpha_{mn}$  = constant in vibration frequency equation  
 $\beta$  = constant in erosive combustion equation  
 $\Gamma$  = surface concentration (concentration of solute at surface)  
 $\gamma$  = deformation due to tangential stress  
 $\gamma$  = specific gravity  $\gamma = \rho \cdot g$   
 $\Delta i_c$  = enthalpy drop  
 $\epsilon$  = relative elongation  
 $\epsilon$  = fraction of condensed portions in primer combustion products  
 $\epsilon$  = porosity  
 $\theta$  = limiting angle  
 $\lambda$  = coefficient of resistance in the falling of a solid body in a liquid  
 $\mu$  = Poisson number

- $\alpha$  = coefficient of adhesiveness
- $Z$  = element number -- atomic number
- $\nu$  = vibration frequency
- $\xi$  = fuel coefficient
- $\pi_p$  = temperature coefficient of pressure
- $\rho$  = density
- $\sigma$  = surface tension
- $\sigma$  = permissible stress on chamber material
- $\sigma_{1,2}$  = interphase tension
- $\sigma_{s,c}$  = liquid-solid body interphase tension
- $\tau$  = cutoff pressure
- $\phi$  = volume fraction of dispersed phase in suspension
- $\phi$  = oxidizer -- combustible component mixture ratio
- $\phi_s$  = oxidizer -- combustible component stoichiometric mixture ratio
- $\phi^*$  = oxidizer -- combustible component mixture equivalent ratio
- $\psi$  = sphericity -- ratio of surface area of sphere with same volume to surface area of particle

#### Abbreviations

- c. w $\bar{r}$ . = density
- c. cz. = molecular weight
- cz. wag. = weight fraction
- t. = temperature
- t.w. = boiling temperature (point)
- t.t. = melting point

#### Translation Editor's Note:

The Polish word "Katalizator" may be translated as either "catalyst" or catalyzer." These two words are used interchangeably in the text, and should not be interpreted to represent two different entities.



## INTRODUCTION

Recent years have seen a considerably increased interest in solid rocket propellants. Many rocket experts believe that by 1970 most if not all rockets used for earth-bound purposes, even intercontinental ballistic missiles, will be powered by solid propellants. In order to achieve this, it will be necessary to overcome a number of difficulties because in some respects solid propellants do not, nor will they ever, equal liquid fuels. Nevertheless, the differences between them must be reduced to a minimum.

One of the fundamental shortcomings of solid propellants is the impossibility of stopping the engine when it is operating and of regulating the fuel consumption during flight (that is, of varying the amount of propellant burned per unit of time).

With respect to the specific impulse and the chemical stability, liquid propellants will always be superior to solid fuels. Solid propellants can never attain specific impulses such as those obtained with  $F_2-H_2$ ,  $O_2-H_2$  and  $O_3-H_2$  mixtures but they can equal other liquid compositions such as, e.g., oxygen-alcohol. The chemical stability of liquid propellants is theoretically unlimited. The oxidizer and the combustible component are prepared and stored separately, which permits them to be preserved for a very long time. On the other hand, in the case of solid propellants, the oxidizer and the combustible component are in direct contact with each other and this leads to decomposition during storage, slowly in some propellants and more rapidly in others. The instability of solid propellants is frequently caused by the instability of the chemical compounds (nitroglycerin, nitrocellulose, etc.) which enter into the composition of these fuels. However, because it is not intended to store these fuels indefinitely, the stability of solid propellants can be increased with certain additives so that they will still be suitable for use after a definite period of time, with only slight changes in their properties with respect to those of a freshly prepared propellant.

Notwithstanding certain disadvantages, solid propellants are superior to liquid fuels in many other respects. One of the most important advantages is the simplicity of construction of the rocket motor. This is comprised of a container, which also serves as the combustion chamber, and a nozzle. The construction of liquid propellant motors must incorporate containers for the oxidizer and the combustible component, a transfer arrangement, a distributing arrangement, a combustion chamber, a cooling arrangement and a nozzle. All this greatly increases the cost of construction and, what is even more important, disadvantageously reduces the ratio of propellant to the total weight of the missile.

The high specific gravity of solid propellants as compared with liquid fuels increases the energy content per unit volume, that is, the so-called specific power. This permits the use of containers with smaller dimensions than those of liquid propellants with the same energy content. Moreover, because the cost of many solid propellants is less than that of liquid fuels, it can be stated that the economy factor would to a great extent, if not entirely, eliminate liquid propellants from terrestrial uses.

The literature contains a great deal of information on the construction of motors for solid propellants and associated theoretical considerations. On the other hand, the chemical side of the problem is frequently mentioned but very little concrete data is offered. The quantitative composition of propellants, particularly the nature of the additives, are frequently industrial or state secrets so that, if they are published at all, it is frequently after several years' delay. Comparatively, the most comprehensive material is still offered by patents, particularly American patents, from which a good deal of valuable information can be obtained after careful examination.

## I. PHYSICO-CHEMICAL FUNDAMENTALS OF SOLID ROCKET PROPELLANTS

### 1. COMBUSTION OF SOLID ROCKET PROPELLANTS

The combustion of solid rocket propellants is based on highly exothermic intermolecular or intramolecular oxidation reactions.

One of the most important characteristics of solid rocket propellants is their rapidity of combustion. The burning rate is the linear velocity at which the solid propellant is consumed and is measured in a direction normal to the propellant surface; it is denoted by "r" and is expressed in cm/sec.

The burning rate depends on the composition and temperature of the propellant, the (chamber) pressure, form and size of the grains of the components (especially the oxidizer), on the degree of homogeneity of the mixture, the rate of flow of gases in the direction tangent to the propellant surface, etc.

With respect to the burning rate, solid propellants can be divided into two groups:

a. Propellants with a burning rate of 0.25-0.4 cm/sec, used for assisted launches, starting turbines in turbojet planes and for producing the compressed gases necessary for conveying the oxidizer and fuel into liquid propellant missiles [1].

b. Propellants with a burning rate from 0.4 cm/sec to several centimeters per second; they are used for rocket propulsion [2].

Quite frequently the two propellant types differ by only small amounts of a substance ("catalyst" of combustion), which often results in a radical change in the burning rate.

With respect to chemical composition and associated physical properties, solid rocket propellants are divided into two groups:

a. Colloidal propellants, which principally contain two basic self-oxidizing substances -- nitrocellulose and one of the liquid nitrates of poly-hydroxy

alcohols (nitroglycerin, nitroglycol, etc.).

b. Composite propellants, in which the predominant portion is the oxidizer, while secondary with respect to quantity is the organic combustible component which simultaneously serves as the oxidizer and binding substance.

### 1.1. Fundamental Laws of Combustion

The interdependence of the burning rate, pressure and temperature is the most important characteristic of any propellant. Theoretical mathematical calculations lead to more or less suitable formulas from the practical point of view, but primarily this interdependence is very complicated. The equation worked out by M. Summerfield and coworkers of Princeton University is one of the most accurate for composite propellants. After certain reductions and at standard temperature, this equation assumes the following form:

$$\frac{1}{r} = \frac{a}{p} + \frac{b}{p^{1.3}}$$
$$\frac{p}{r} = a + bp^{0.3}$$

where  $r$  is the burning rate,  $p$  the pressure and  $a$  and  $b$  the constants for the given propellant.

The curve with coordinates  $p/r$  and  $p^{2/3}$  is almost linear. Intersection with the  $p/r$  axis gives the  $a$  value, while  $b$  is defined by the slope [2].

Although the above dependence is the preferred one, empirical equations are in general use because of their earlier formulation, wider recognition and simpler form, and also because of their broader application (they apply also to colloidal propellants as well as composite ones).

The basic empirical equation is

$$r = ap^n \tag{1.1}$$

or

$$r = a + bp^n$$



where:  $a$  and  $b$  are constants for the given propellant, and  $n$  is an exponential constant for the given propellant within a certain pressure range.

This dependence frequently is not fulfilled in the case of a wide range of pressures; then it so happens that the exponent  $n$  is different at different pressures for the same propellant.

It is necessary for the pressure exponent  $n$  to be less than one because at values close to  $n = 1$ , a stable combustion is impossible. This means that an incidental slight increase in pressure causes a tremendous increase in the burning rate and, consequently, the fuel consumption (or the mass of combustion products generated in a unit of time), several times greater than the output of the engine nozzle, i.e., than the limiting amount of gases that can be discharged by the nozzle per unit of time. Then a violent pressure increase takes place in the combustion chamber and the engine breaks apart.

It is most preferable that the exponent  $n$  be equal to 0, because then the burning rate is not a function of the pressure. However, it is very difficult and not always possible to obtain fuels with such properties. Therefore, it is recommended that the exponent at least be less than 0.65 [1]; however, there frequently are fuels with an exponent  $n$  going as high as 0.9.

The exponent  $n$  can be determined by finding at least two values of the burning rate at two different pressures [3]:

$$r_1 = a p_1^n \quad \text{and} \quad r_2 = a p_2^n$$

and then

$$\frac{r_1}{r_2} = \left( \frac{p_1}{p_2} \right)^n \quad \text{or} \quad \frac{\log \frac{r_1}{r_2}}{\log \frac{p_1}{p_2}} = n = \frac{\log r_1 - \log r_2}{\log p_1 - \log p_2}.$$

If the burning rate is known for standard pressure conditions, i.e., under a pressure of  $70.3 \text{ kg/cm}^2$  (this figure results from the conversion of pressure values

taken as standard by American scientists, 1000 lb/cal<sup>2</sup> units, to kg/cm<sup>2</sup> units, then

$$r_1 = r_{70} \left( \frac{p_1}{70} \right)^n \quad r_1 = \left( \frac{r_{70}}{70^n} \right) p_1^n$$

whence

$$a = \frac{r_{70}}{70^n} \quad \text{and} \quad n = \frac{\log r_1 - \log r_{70}}{\log p_1 - \log 70}$$

The constants  $a$  and  $n$  are thus designated.

All the above equations are valid for fuels with unvarying temperatures, or for  $t = a$  constant.

The most general equation incorporating the temperature dependence is

$$r = bp^n e^{\pi_p(T'-T)} \quad (1.2)$$

where:  $b$ ,  $n$  and  $\pi_p$  are constants in the given pressure and temperature range,

$\pi_p$  is the temperature sensitivity to the pressure, otherwise called the temperature coefficient of the pressure,

$T'$  is the standard temperature, and

$T$  is the actual temperature [4].

It is easy to see that for  $T = \text{constant}$  and  $(T' - T) = \text{constant}$  and

$$be^{\pi_p(T'-T)} = \text{const}$$

the equation (1.2) assumes the form of equation (1.1), where

$$a = be^{\pi_p(T'-T)}$$

On the other hand, when the standard temperature  $T' = T$ , that is, when  $T' - T = 0$ , the constant  $a = b$ . It results from this that the equation  $r = ap^n$  is a special case of equation (1.2).

The temperature coefficient of the pressure  $\pi_p$  is defined as the ratio of the percent pressure variation to the temperature variation of the fuel in unit values

$$\pi_p = \frac{\text{percent pressure variation}}{1^\circ\text{C (fuel temperature)}}$$

$$\pi_p = \frac{\Delta p \frac{100}{p}}{\Delta T} \quad [t^{-1}]$$

The formulated equation also became the temperature coefficient of the burning rate  $u$ . This is the ratio of the percent burning rate variation at constant pressure to the fuel temperature variation in unit values

$$u = \frac{\text{percent burning rate variation}}{1^\circ\text{C (fuel temperature)}}$$

$$u = \frac{\Delta r \frac{100}{r}}{\Delta T} \quad [t^{-1}]$$

There is an interdependence between  $n$ ,  $\pi_p$  and  $u$

$$\pi_p = \frac{u}{1 - n}$$

whence

$$n = 1 - \frac{u}{\pi_p}$$

or

$$n = \frac{\pi_p - u}{\pi_p} \left[ \frac{t^{-1}}{t^{-1}} = 1 \right]$$

the value of the exponent  $n$  is not uniform [5].

For example: a composite fuel with 25% polyester combustible component and 75%  $\text{NH}_4\text{ClO}_4$  has  $u = 0.25[t^{-1}]$  and  $\pi_p = 0.45[t^{-1}]$ . It follows that the burning rate increases 0.25% and the pressure 0.45% when the fuel is heated  $1^\circ\text{C}$ .

The relationships (1.1) and (1.2) are valid only for certain temperature and pressure ranges. As already mentioned, some fuels can attain the exponent value  $n = 0$  within a certain pressure range; this means that the burning rate ceases to

be a function of the pressure and becomes constant. This is called the plateau effect and is most frequently encountered in colloidal propellants when small amounts of lead salts are inserted [6]. This effect is also possible in composite fuels with ammonium perchlorate and with certain additives.

It can also occur that the exponent  $n$  assumes a negative value for some pressure ranges; in other words, the burning rate decreases with increasing pressure. This is called the mesa effect [7]. Both of these effects are illustrated in Figure 1.1.

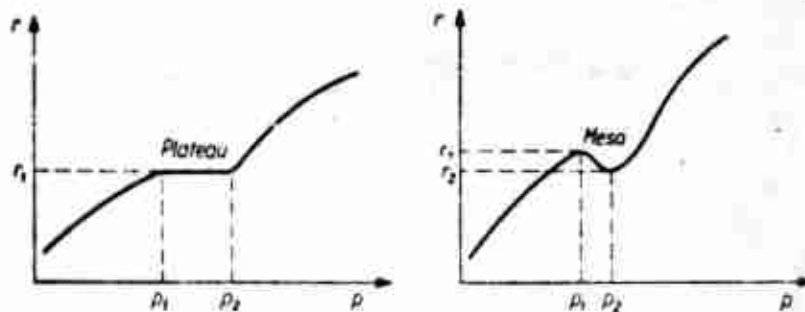


Figure 1.1. The plateau and mesa effects which arise during the burning of some solid rocket propellants.

It quite frequently occurs that the burning rate is so low under atmospheric pressure that the burning fuel is extinguished. In this case, a pressure increase is necessary for regular, stable combustion. This pressure increase is obtained by burning a small auxiliary charge, the burning time of which is of the order of a few hundred milliseconds (usually about 500).

At the present time the burning rate and the coefficients  $n$ ,  $\pi_p$  and  $u$  can be influenced by means of various additives. Thus, the following can now be expected of fuels:

- (a) definite limits of the burning rate,
- (b) a definite effective burning rate,
- (c) low and high exponents  $n$ ,
- (d) a low  $\pi_p$  value,
- (e) a calm ignition,

- (f) a high combustion productivity,
- (g) elimination of unstable combustion, and
- (h) elimination of detonations.

Although the mechanisms of burning rate variation are presently more or less well known, the mode of action of additives on the variation of  $n$ ,  $u$  and  $\pi_p$  is either cloaked in secrecy or is still in the research stage.

## 1.2. The Mechanism of Combustion

The burning of solid rocket propellants is based on a number of complex exothermic chemical reactions of decomposition as well as oxidation and reduction. These reactions initiate a pyrolytic effect in the thin layer just under the combustion surface. The combustion process is complete when a thermodynamic equilibrium in the gaseous phase is achieved.

Particular burning mechanisms are very complex and are difficult to study. Moreover, they are different for colloidal and for composite fuels. In the case of colloidal propellants, the substance burned is homogeneous and, in particular, the components are most frequently self-oxidizing. Therefore, exothermic decomposition reactions will predominate here. In the case of composite fuels, the substance is nonhomogeneous and the predominant constituents are an oxidizer and a combustible component; consequently, oxidation and reduction reactions between the decomposition products of both constituents will constitute the majority of transformations taking place.

The burning diagram for colloidal fuels is presented most simply in Figure 1.2. These fuels are homogeneous substances; most of the constituents are cellulose nitrates and poly-hydroxy alcohols. The area in which the burning reactions take place can be divided into several layers parallel to the combustion surface. The sub-surface zone is located immediately below the combustion surface, otherwise called the decomposition zone because a partial decomposition of the organic nitrates takes place here due to the effect of temperature. This decomposition



becomes more substantial in the foaming zone (also called the fizzing zone), during which large amounts of nitrogen dioxide and other gaseous products are liberated.

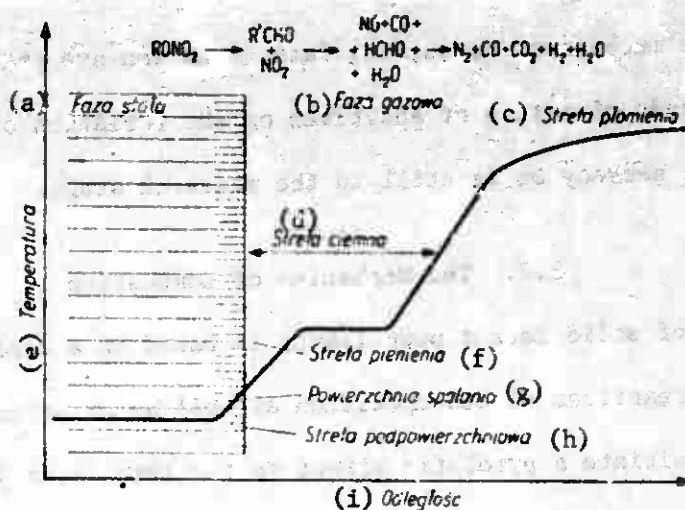


Figure 1.2. Combustion diagram for colloidal fuels.

Key: (a) = solid phase; (b) = gaseous phase; (c) = flame zone; (d) = dark zone; (e) = temperature; (f) = foaming zone; (g) = combustion surface; (h) = subsurface zone; and (i) = distance.

Reactions in the gaseous phase begin at this moment. First, activated products are generated without heat production; this is the so-called dark zone or preparation zone. Then exothermic reactions take place, a whole series of excited atoms and molecules arise and produce luminescence by radiating an abundance of energy in the form of quanta. This is the flame zone.

The thickness of the subsurface layer is a function of the burning rate and the penetrability of the fuel to radiation from the flame zone. With higher burning rates and lesser penetrability, this layer is thinner. As the combustion surface is approached in the direction of the gaseous phase, the temperature increases due to the exothermic decomposition reaction, radiation absorption and thermal conduction and reaches about 300°C in the foaming zone, after which it increases violently to about 1400°C, acquiring its highest value in the flame zone.

The thickness of the foaming zone is a function of the volume of gases liberated. Thus, it is not surprising that this layer is very thin in the case of

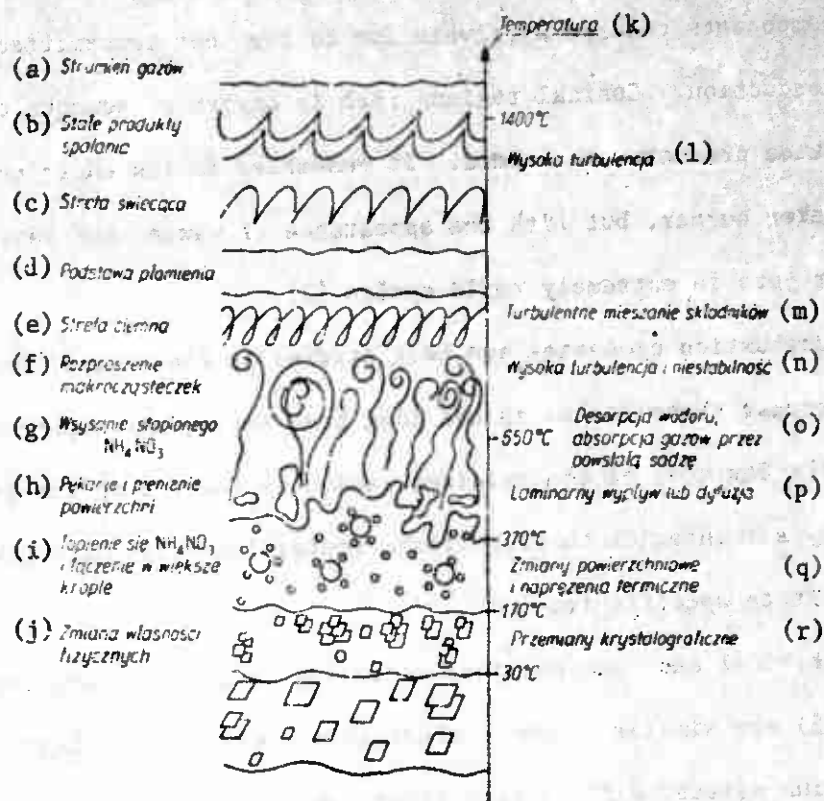


Figure 1.3. Physical effects arising during the combustion of fuels containing ammonium nitrate. Key: (a) = gas stream; (b) = solid combustion products; (c) = luminous zone; (d) = flame base; (e) = dark zone; (f) = macromolecular diffusion; (g) = absorption of molten  $\text{NH}_4\text{NO}_3$ ; (h) = cracking and foaming of the surface; (i) = fusion of  $\text{NH}_4\text{NO}_3$  and association into larger drops; (j) = modification of physical properties; (k) = temperature; (l) = high turbulence; (m) = turbulent mixing of the components; (n) = high turbulence and instability; (o) = hydrogen desorption, gas absorption by the evolved carbon black; (p) = laminar outflow or diffusion; (q) = surface changes and temperature stresses; and (r) = crystallographic transformations.

higher pressures. The same applies to the preparation zone. The thickness of this zone increases rapidly with decreasing pressure and it may happen that the activated product concentration becomes inadequate, the flame zone wanes and, although the grain undergoes decomposition, the combustion is incomplete [7,8].

The combustion mechanism of composite propellants is completely different. This, of course, is due to the inhomogeneity of the fuel. The entire propellant

surface is composed alternately of strips of oxidizer and combustible component. The two components undergo pyrolysis due to the heat transmitted by radiation or thermal conduction. Conical regions rich in oxygen or gaseous combustible component decomposition products are formed. It resembles in its entirety the burning of gases in a Meker burner, but with the appearance of waxing and waning of individual streams or jets in extremely rapid cycles [2].

The combustion processes are best studied in the case of fuels with ammonium nitrate because these fuels, as has long been known, are superior to others with respect to the low cost of the oxidizer (which is the reason for its common use), although they are inferior to propellants containing other oxidizers ( $\text{NH}_4\text{ClO}_4$ ,  $\text{LiNO}_3$ ) with respect to specific impulse.

The physical and some chemical processes of combustion of most composite fuels (Figure 1.3) are similar to the combustion of fuels containing ammonium nitrate [4].

Ammonium nitrate differs from other commonly used oxidizers by its low melting point ( $169.6^\circ\text{C}$ ). Thus, when fuels containing ammonium nitrate are heated above  $170^\circ\text{C}$ , the molten oxidizer breaks away from the combustible component, tears bits of it away and is expelled from the surface together with the gaseous products.

A number of processes absorb certain amounts of energy, which undoubtedly makes combustion more difficult. Thus, for example, large particles must undergo decomposition, large molecules must also be decomposed and the products formed require an additional amount of energy upon being mixed and heated to the activation level. A portion of the energy is also expended in expulsion from the surface, in the transfer of material, etc.

From the chemical point of view the combustion processes of composite fuels are different primarily through the employment of different oxidizers. Because the combustible components enter into the composition in the form of the same elements (C, H, O, N -- more rarely S and Cl), they are not as decisively significant. At the very most, they can influence the equilibrium state of some reactions in one or the other direction.



Chemical combustion processes, particularly, (Figure 1.4) are most evident in fuels containing ammonium nitrate [4].

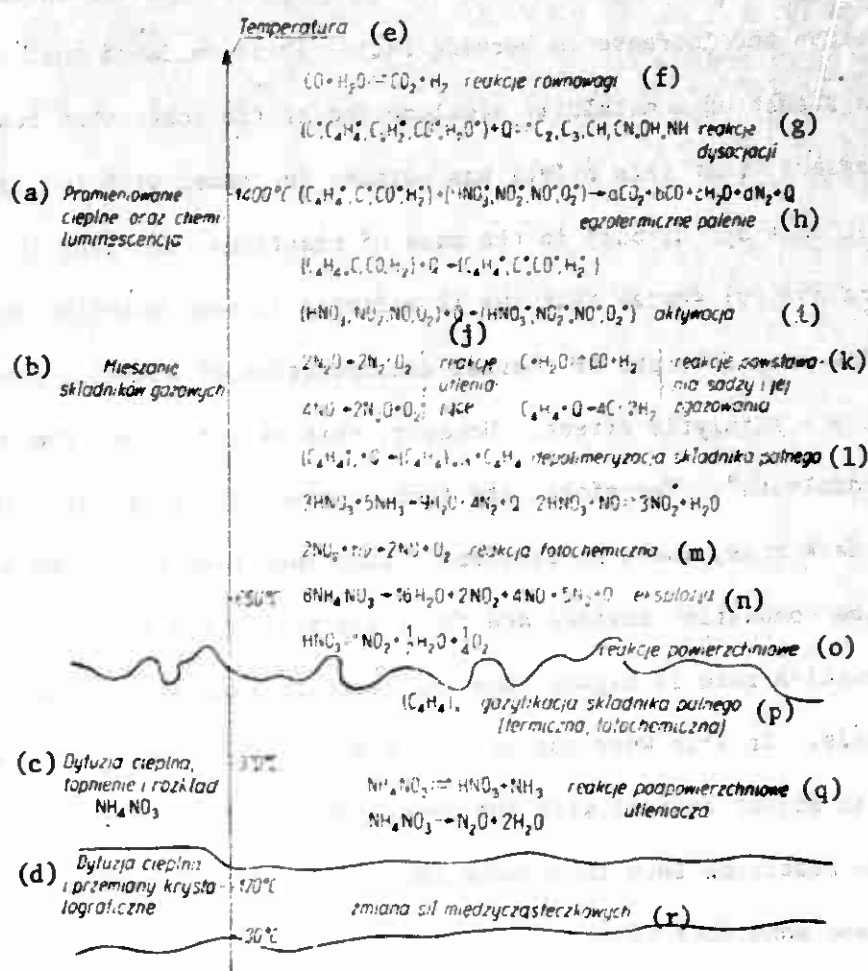


Figure 1.4. Chemical combustion processes of propellants containing ammonium nitrate and a combustible component of composition  $(\text{C}_4\text{H}_4)_x$ . Key: (a) = thermal radiation and chemiluminescence; (b) = gaseous component mixing; (c) = thermal diffusion, fusion and decomposition of  $\text{NH}_4\text{NO}_3$ ; (d) = thermal diffusion and crystallographic transformations; (e) = temperature; (f) = equilibrium reactions; (g) = dissociation reactions; (h) = exothermic combustion; (i) = activation; (j) = oxidation reaction; (k) = reactions of carbon black formation and its gasification; (l) = combustible component depolymerization; (m) = photochemical reaction; (n) = explosion; (o) = surface reactions; (p) = gasification of the combustible component (thermal, photochemical) (q) = subsurface oxidizer reactions; and (r) = modifications of intermolecular forces.

### 1.3. The Action Mechanisms of Combustion "Catalysts"

It has long been asserted that small amounts of certain substances have a radical effect on the increase in burning rate. It is believed that this effect arises only as a result of a catalytic acceleration of the combustion reaction. V. K. Getman [4] asserts that this effect has nothing in common with the catalytic action. Indeed, it does appear only in the case of reactions unfolding in the gaseous phase. Kenji Kuratani [9] states that the 1% addition of some metallic oxides can accelerate or slow down the rate of thermal decomposition of ammonium perchlorate. This is undoubtedly a catalytic effect. However, this effect is not the only mode of action of the "catalysts". Therefore, the term, combustion "catalyst", is not an apt one.

The dark zone, where no exothermic reactions take place, is believed to exist between the combustion surface and the flame zone. The fact that the grain gasification reaction rate is higher than the reaction rate in the flame zone bears witness to this. If this were not so, there would be no dark zone and the flame zone would be in direct contact with the combustion surface. The rate of surface and subsurface reactions then influences the burning rate directly, but the burning rate in the flame zone does not.

The combustion "catalysts" act in different ways. Some develop their action exothermically on the combustion surface and supply heat directly to the surface reactions, others act to break down the surface by means of physical changes, others, on the other hand, by means of excitation in the flame region, emit high-energy quanta, capable of photolysis of the propellant, and others then catalytically accelerate the breakdown of the oxidizer.

Thus, there are 4 ways that "catalysts" can influence the combustion process:

1. radiation,
2. exothermic decomposition,
3. catalytic decomposition of the oxidizer, and
4. physical transformations.

Most frequently, all four methods act simultaneously, but to different degrees.

### Radiation

If the predominant factor is "catalyst" influence on the transfer of energy to the combustion surface by radiation, then at least a certain portion of the energy supplied without the "catalysts" must come from the radiation. Actually, the study of colloidal fuels suggests that radiation participation in energy transfer amounts to 10-20%. This radiation comes from the visible region and the photon energy is in equilibrium with the flame temperature. On the other hand, "catalysts" exerting their influence by radiation contain atoms capable of photon emission of energy much greater than the energy of thermal radiation. Thus, for example, photons with a wavelength coinciding with the 5167 Å iron lines have sufficient energy to break the bonds of the polymer by photolysis. Such photons produce depolymerization by breaking the spatial lattice bonding.

Photon absorption by gas molecules has little significance with the exception of  $\text{NO}_2$ , which has a high adsorption ability, and the fuel molecules, from which hydrogen is dissociated.

Colloidal propellants proved to be quite penetrable for radiation, whereby not only the subsurface layer but also further portions of the charge are subjected to heating. This may be the reason for pyrolysis of the deeper layers of the charge, which leads to cracking, unstable combustion and even explosions. In order to avoid this, the grain penetrability is reduced by the addition of certain amounts of soot, which stops most of the radiation in the subsurface layer without further penetration.

In the case of composite fuels, the photons penetrate the gaseous layer and strike the fuel. If they reach the molten oxidizer, they are absorbed to a small degree, some are reflected and the remainder continue on to the combustible component. Consequently, it is not difficult to understand why the combustible component absorbs the major portion of the radiation, i.e., at least 60%, in spite of the fact

that it has a much smaller surface area than the oxidizer.

The radiation of higher energy photons is caused by the substance not being in equilibrium or by chemiluminescence. In the absence of excited "catalyst" atoms, these substances can be unstable molecules or radicals  $C_2$ ,  $C_3$ ,  $CH$ ,  $OH$ ,  $CN$ ,  $NH$  and others. The  $C_2$  molecule, which appears in the flame in rather large amounts, is of particularly great importance.

Everything points to the fact that photolysis is a very important factor and that the atoms of the metallic elements, which influence the burning rate, act precisely in the above manner. It is no mere coincidence that the atoms exhibiting the greatest chemiluminescence, Fe, Cu, Co, Ni, K, Pb..., also have the greatest influence on the burning rate.

#### Exothermic decomposition

It has been found that chromium does not exhibit much chemiluminescence, yet its compounds are used as combustion "catalysts". The metal itself has no influence in this respect. On the other hand, the chromium oxides, chromates, dichromates, polychromates and chromites have a high radiation absorption capability and thus supply energy to surface reactions. Ammonium dichromate has long been used in photography because of its good radiation absorption. The chromates, dichromates and polychromates are the most effective in this respect because, in addition to the absorbed energy, they also have high heats of dissociation. For example, ammonium dichromate has a heat of dissociation which is more than 5 times greater than that of ammonium perchlorate (into the elements) (420.07 kcal/mol and 78.3 kcal/mol, respectively).

#### Catalytic decomposition of the oxidizer

As already stated, some metal oxides accelerate the thermal decomposition of ammonium perchlorate.  $CuO$ ,  $ZnO$ ,  $Cr_2O_3$  are the most effective;  $MnO_2$  and  $MgO$  have average effectiveness and  $Al_2O_3$ ,  $Fe_2O_3$  and  $TiO_2$  have minor effectiveness.  $V_2O_5$  exhibits an inhibiting action. Furthermore, in the presence of different oxides,

gaseous products having different compositions arise [9].

#### Physical transformations

In the case of a low melting oxidizer ( $\text{NH}_4\text{NO}_3$ ) and a readily decomposing combustible component, a certain amount of liquid and gaseous substances arise inside the fuel; as the temperature increases, these substances act more and more strongly to break down the surface. Crystallographic transformations, which always bring about a volume increase when the temperature is increased, have this same activity. Differences in the coefficients of thermal expansion between the oxidizer and the combustible component cause many surface cracks. All these surface changes have a great influence on acceleration of the combustion [4].

In summarizing the above, it can be stated that:

- a. Because the thermal radiation is in equilibrium with the temperature of the flame, it cannot be a dominating factor in the transfer of energy "down" to the combustion surface, nor can it be disregarded altogether.
- b. Radiation in a state lacking in equilibrium, or chemiluminescence, can be a dominating factor in a fuel-rich flame, especially in the presence of "catalysts".
- c. Chemiluminescence and, to a lesser degree, thermal radiation can supply energy for the photolytic decomposition of the combustible component, in addition to the pyrolysis occurring on the surface.
- d. Heat supplied by radiation, thermal conduction and exothermic subsurface reactions leads to a pyrolytic decomposition of the oxidizer, accelerated by the catalytic action of metallic oxides.
- e. The physical factor assumes a greater significance and is decisive in the final decomposition of the surface layer only when the combustion surface is weakened by the above processes.

#### 1.4. Thrust and Specific Impulse

Before endeavoring to formulate the composition of a solid propellant, the ballistic, thermodynamic and mechanical requirements of the fuel should be known.

Some of these characteristics can be predicted, at least approximately, by learning the influence of the particular components on the parameters of the finished propellant.

One of the principal parameters of rocket fuels is the specific impulse, denoted by the symbol  $I_g$ . The specific impulse of the fuel can be determined on the basis of experimental studies and theoretical calculations. The theoretical calculations can be carried out on the basis of laws for the conversion of chemical energy to other forms of energy.

During the combustion process the chemical energy is converted into thermal energy, radiation energy and potential energy.

The radiation energy goes partially into heating the engine walls (conversion to heat), is partially diffused outward in the form of luminous gas streams and is partially absorbed by the burning material, exciting it to continue burning. The results of some studies indicate that for certain fuels the energy passing from the combustion zone to the fuel zone is transferred chiefly by radiation.

Most of the energy liberated during the burning process consists of heat energy, which is partially wasted in heating the engine and surroundings as well as on the dissociation reaction, which takes place at high temperatures. Potential energy arises from the high pressures that develop in the combustion chamber when the engine is operating. As a result of gas expansion, the thermal and potential energies are transformed into kinetic energy due to the high velocity of the combustion products as they are expelled from the nozzle. Due to the effect of the combustion gases leaving the nozzle of the engine, a thrust force acts on the rocket in a direction opposite to that of the discharging gases.

The amount of thrust developed is the value of greatest interest to us during the flight of the rocket.

According to Newton's laws of dynamics, this force is equal to the product of the mass (of expelled gases) and the acceleration



$$F = ma$$

(1.3)

where

$$a = \frac{W_1 - W_0}{t}$$

$F$  = thrust,

$m$  = mass of expelled gases,

$a$  = acceleration,

$W_1$  = final (maximum) velocity of the expelled gases,

$W_0$  = initial velocity

$t$  = action time of the acceleration.

Because the gas velocity is measured in relation to the engine, the initial velocity equals zero, since at the moment of burning (generation) of the gases, the engine and the propellant consist of one single unit. Accordingly

$$a = \frac{W_1}{t} \quad \text{and} \quad F = m \frac{W}{t}$$

(in this form the index on  $W$  can be omitted) or

$$F = \frac{m}{t} W$$

The ratio  $m/t$  is called the mass output and is designated by  $G = m/t$ . Thus, this is the mass output of the fuel per unit of time. The mass output is a variable value; therefore, the following expression will be valid

$$F = W \frac{dm}{dt} \quad (1.4)$$

The mass output  $G = m/t$  can be readily determined on the basis of the fact that the output of combustion products in the nozzle is equal to the decrease in mass of

the burning fuel.

Knowing the burning rate, specific gravity and combustion surface of the solid propellant, we calculate  $G$  from the equation

$$G = A_{sp} r \gamma \quad (1.5)$$

where:  $A_{sp}$  = combustion surface of the charge,

$r$  = burning rate,

$\gamma$  = specific gravity of the fuel.

The thrust should be specified in units of force -- kg, and from the components of thrust (m/sec)·(kg/sec) we have mkg/sec<sup>2</sup>, which is a multiple of the physical unit of force, the dyne. In order to convert the physical units to mechanical units, the physical units must be divided by the conversion coefficient 9.81, which is precisely the value of acceleration due to gravity, denoted by  $g$ .

Finally then

$$F = \frac{Wm}{gt} \quad (1.6)$$

where:  $m$  and  $t$  are known from the burning rate and the geometric form,

$g$  is a constant for a given altitude with respect to sea level.

Accordingly, the derivation of the equation in  $W$  remains in the expression (1.6); we derive this from the equation of the conservation of energy of flow.

The total energy of flow of a given gas is composed of the following components:

1. the internal energy,  $c_v T$ , where:  $c_v$  = the specific heat at a constant volume and  $T$  = the absolute temperature of the gas;
2. the chemical energy,  $U_{ch}$ ;
3. the kinetic energy of flow,  $W^2/2g$ ;
4. the potential energy of pressure  $pV$  ( $p$  = pressure; and  $V$  = volume).

We assume that there is an adiabatic, linear flow of a chemically neutral gas



mixture with no friction on the walls. Assuming that heat is not supplied to or removed from the flow during the passage, the total flow energy  $E$  will be a constant

$$c_p T + A p V + U_{ch} + A \frac{W^2}{2g} = E = \text{const} \quad (1.7)$$

where  $A$  is the heat equivalent of work, which is used in converting kg to kcal

$$A = \frac{1}{427} \frac{\text{kcal}}{\text{kg}}.$$

The equation (1.7) is sometimes called the thermodynamic Bernoulli gas equation.

In order to simplify expression of the energy it should be noted that  $c_p T + A p V + U_{ch}$  represents the total enthalpy  $i_c$  of the gas mixture, then the equation (1.7) may be written in the form

$$i_c + A \frac{W^2}{2g} = \text{const} \quad (1.8)$$

It follows from the above that the kinetic energy increase of gases is equal to the drop in the total enthalpy, as takes place between two gas flow sections

$$\frac{A}{2g} (W^2 - W_1^2) = i_{c1} - i_{c2}$$

hence

$$W = \sqrt{W_1^2 + \frac{2g}{A} \Delta i_c}.$$

If we take the combustion surface of the fuel charge as the initial section,  $W_1 = 0$ , then

$$W = \sqrt{\frac{2g}{A} \Delta i_c} \quad (1.9)$$

It remains to find the expression in an accessible form in  $\Delta i_c$ . During the

expansion of the chemically neutral gas, the change in enthalpy is expressed by a change in the temperature and the specific heat

$$\Delta i_c = c_p \Delta T \quad \Delta i_c = c_p (T_2 - T_1) \quad (1.10)$$

where  $c_p$  is the specific heat of the gas under constant pressure, or

$$-\Delta i_c = c_p (T_1 - T_2) \quad (1.11)$$

In the case of the adiabatic transformation of gases

$$\frac{T_2}{T_1} = \left( \frac{p_2}{p_1} \right)^{\frac{k-1}{k}} \quad ; \quad T_2 = T_1 \left( \frac{p_2}{p_1} \right)^{\frac{k-1}{k}} \quad (1.12)$$

where

$$k = \frac{C_p}{C_v} = \frac{C_v + AR}{C_v} = 1 + \frac{AR}{C_v} \quad (1.13)$$

$k$  = the adiabatic constant,

$C_v$  = the molar heat of a gas at a constant volume,

$C_p$  = the molar heat of a gas under constant pressure.

It follows from (1.13) that

$$C_v = \frac{1}{k-1} AR \quad C_p = \frac{k}{k-1} AR \quad (1.14)$$

It is well known that the relation of the specific heat to the molar heat has the form

$$c_p = \frac{C_p}{M} \quad c_v = \frac{C_v}{M}$$

$M$  = molecular weight of the gas.

After substitution of the molar heat value from (1.14), we obtain

$$c_p = \frac{k}{k-1} \frac{AR}{M} \quad c_v = \frac{1}{k-1} \frac{AR}{M} \quad (1.15)$$

By substituting the (1.12) and (1.15) values in the equation (1.11), we obtain

$$- \Delta i_c = \frac{k}{k-1} \frac{AR}{M} \left[ T_1 - T_2 \left( \frac{p_2}{p_1} \right)^{\frac{k-1}{k}} \right] \quad (1.16)$$

or

$$- \Delta i_c = \frac{k}{k-1} \frac{ART_1}{M} \left[ 1 - \left( \frac{p_2}{p_1} \right)^{\frac{k-1}{k}} \right] \quad (1.17)$$

(subsequently, the minus sign in  $\Delta i_c$  will be omitted).

By substituting the last equation in (1.9), we obtain

$$W = \sqrt{2g \frac{k}{k-1} \frac{RT_1}{M} \left[ 1 - \left( \frac{p_2}{p_1} \right)^{\frac{k-1}{k}} \right]} \quad (1.18)$$

When equation (1.18) is used, it should be kept in mind that it is valid for all the preceding assumptions and therefore for the adiabatic transformation (i.e., when a heat exchange with the environment does not take place), if the expanding gases are chemically neutral (i.e., the gas composition does not change in passing from section 1 to section 2 (Figure 1.5)), and for the flow without friction of the gases on the chamber walls. The velocity calculated in this manner is not exact and is usually higher than the true value by about 5%. However, keeping this in mind, the above equation can be used in orientational theoretical computations of the projected fuel. However, before equation (1.18) is used in calculating the impulse, elementary considerations must be taken into account.

It follows from equation (1.18) that the gas efflux velocity is proportional to the square root of the combustion temperature and increases with increasing difference in the pressure of the gases in the combustion chamber ( $p_1$ ) and in the

discharge from the nozzle ( $p_2$ ). An explanation of the indices of the individual parameters can be found in Figure 1.5.

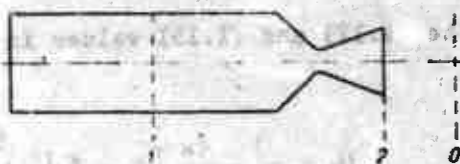


Figure 1.5. Parameter designation diagram for the engine during combustion.

For the sake of simplification, it is assumed that the pressure in the entire combustion chamber is constant. In reality, there is a fixed pressure difference between the front and back portions of the chamber during the entire burning time. This difference changes during the burning and is different for particular conditions, which is of course reflected in the burning process itself. However, when considering the largeness of the thrust, an average pressure value can be assumed and a sufficient accuracy can be obtained. The influence of the pressure difference between the front and rear portions of the chamber on the burning process will be discussed further in subsequent chapters.

In order that a maximum pressure decrease may take place, the gas must expand to the ambient pressure  $p_0$  upon discharge from the nozzle. For a given  $p_0$ , in practice, the nozzle can be constructed in such a manner that  $p_0 = p_2$ , but taking the fact that the rocket engine operates at different altitudes (different  $p_0$  values) into account, the engine can function under maximum expansion exploitation conditions only for some definite brief period of time. As  $p_0$  decreases, the sectional surface area of the nozzle must be increased during flight in order to obtain a maximum gas expansion, and this is difficult to accomplish<sup>1</sup>. If we assume that for each  $p_0$  value we have an adapted nozzle, in which a maximum expansion takes place

<sup>1</sup>See page 86.

in section 2, then a higher gas discharge velocity can be expected for a lower environmental pressure.

The maximum discharge velocity is attained when the engine is functioning in interplanetary space, when  $p_0 = p_2 \approx 0$ .

Then

$$W_{max} = \sqrt{2g \frac{k}{k-1} \frac{RT_1}{M}} \quad (1.19)$$

The third basic value (in addition to the temperature and the pressure) upon which the discharge velocity of the combustion products depends is the molecular weight of these products. The discharge velocity is inversely proportional to the square root of this weight.

By employing equation (1.19), we can calculate the maximum thrust, maximum impulse and maximum specific impulse. These maximum characteristic values of the engine are not attainable in practice (rocket engines seldom operate under  $p_0 \approx 0$  conditions). Calculations of the so-called ideal impulse and ideal specific impulse are closer to the true state of affairs. When calculating these values, it is assumed that the environmental or ambient pressure

$$p_0 = p_2 = 1 \text{ atm.}$$

Thus, this is a calculation of the function of an engine under pressure conditions corresponding to the pressure at sea level and with a nozzle permitting the expansion of gases to 1 atm upon their discharge.

In summarizing, it should be stated that there are concepts of the real velocity of the escaping gases, the maximum velocity, the ideal velocity and the velocity resulting from experimental thrust measurements. Corresponding to these velocity concepts, there are thrust, impulse and specific impulse concepts.

By applying equation (1.18) to equation (1.6), we obtain

$$F = \frac{m}{gt} \sqrt{\frac{2g}{k-1} \frac{k}{M} \frac{RT_1}{M} \left[ 1 - \left( \frac{p_2}{p_1} \right)^{\frac{k-1}{k}} \right]} \quad (1.20)$$

After reformation, we obtain

$$F = G \sqrt{\frac{2k}{g(k-1)} \frac{RT_1}{M} \left[ 1 - \left( \frac{p_2}{p_1} \right)^{\frac{k-1}{k}} \right]} \quad (1.21)$$

By integrating the thrust over time, we obtain the total engine impulse I

$$I = \int_0^t F dt \quad (1.22)$$

This equation is used in working out experimental results; when the thrust curve over time is known, it is integrated and the total impulse is obtained.

In order to obtain a practical equation in theoretical calculations, we assume that the thrust is constant during its time of action. Then

$$I = Ft \quad (1.23)$$

By substituting F from (1.20), we obtain

$$I = m \sqrt{\frac{2k}{g(k-1)} \frac{RT_1}{M} \left[ 1 - \left( \frac{p_2}{p_1} \right)^{\frac{k-1}{k}} \right]} \quad (1.24)$$

As stated in the introduction, the specific impulse  $I_s$  is the most important parameter for the characteristics of a propellant.

$$I_s = \frac{I}{m} = \sqrt{\frac{2k}{g(k-1)} \frac{RT_1}{M} \left[ 1 - \left( \frac{p_2}{p_1} \right)^{\frac{k-1}{k}} \right]} \quad (1.25)$$

It follows from equation (1.23) that I is measured in kg·sec, and  $I_s$  is obtained by dividing the total impulse by the mass of the total fuel, expressed in kg. Therefore,  $I_s$  is measured in kg·sec/kg, which is usually written as sec, although



this term is not technically correct. Thus, the specific impulse denotes the kilogram-second impulse that can be obtained by burning 1 kg of fuel. The specific impulse is greater for most liquid propellants than for solid fuels and frequently exceeds 300 sec, while for the best solid propellants, it is not much more than 250 sec.

In choosing a fuel, however, one cannot be guided only by this indicator. The specific gravity of the fuel is an important factor. A higher specific gravity permits the "fitting" of a greater impulse in a small volume, even when  $I_g$  is relatively small. This is the case with solid propellants, the specific gravity of which is advantageous in comparison with liquid fuels. The volume concept of the specific impulse, sometimes called the specific density impulse, is sometimes given for comparison

$$I_{sob} = I_{sy} [\text{kg} \cdot \text{sec} / \text{dcm}^3] \quad (1.26)$$

For example, if we have a liquid fuel with its  $I_g$  as high as 300 and a specific gravity of 1, and a solid propellant with  $I_g = 200$  and a specific gravity of 1.5, their volume impulse will be equal to 300. The specific impulse of some commonly used solid rocket propellants is given in Table 1.1.

It is evident from the table that the most important fuels are those based on ammonium perchlorate, taking into account the availability of the raw materials and the specific impulse. When a high-energy combustible component and other additives (e.g., light metals) are chosen, ammonium perchlorate-based propellants can attain a specific impulse as high as 270 sec.

Because potassium perchlorate has a greater specific gravity than ammonium perchlorate, it can furnish a sufficiently large specific volume impulse, although the specific weight impulse is considerably less than the impulse of propellants with ammonium perchlorate. Ammonium nitrate-based propellants have a considerably smaller weight and volume specific impulse than the two preceding ones; nevertheless, they may be chosen because of the low cost of the raw material.



TABLE 1.1. SPECIFIC IMPULSES OF THE MORE IMPORTANT SOLID PROPELLANTS

Composition	Specific impulse (sec)
<u>Composite propellants</u>	
NH <sub>4</sub> ClO <sub>4</sub> + polyester resin	180-200
NH <sub>4</sub> ClO <sub>4</sub> + polyvinyl chloride	225
NH <sub>4</sub> ClO <sub>4</sub> (60%) + polyurethan (25%) + other additives (15%)	240
NH <sub>4</sub> ClO <sub>4</sub> + polybutadiene	250
Oxidizer (65%) + nitropolyurethan	250
NH <sub>4</sub> ClO <sub>4</sub> + polyisobutylene + decaborane	260
Oxidizer + polyurethan + light metals	270
KClO <sub>4</sub> + asphalt	180-195
KClO <sub>4</sub> + (C <sub>2</sub> H <sub>2</sub> O) <sub>n</sub>	165-210
NaNO <sub>3</sub> + ammonium picrate + binder	180
NH <sub>4</sub> NO <sub>3</sub> + (C <sub>2</sub> H <sub>4</sub> O) <sub>n</sub>	195
LiClO <sub>4</sub> + various binders	250-300
<u>Colloidal propellants (%)</u>	
<u>extruded</u>	
Nitrocellulose	50-60
Nitroglycerine	30-45
Plasticizer	1-10
<u>cast</u>	
Nitrocellulose	45-55
Nitroglycerine	25-40
Plasticizer	10-25

Although lithium perchlorate-based propellants have the greatest specific impulse, they cannot be chosen because the raw materials are expensive and difficult to obtain. As can be seen in Table 1.1, colloidal fuels can equal composite fuels in many cases with respect to the specific impulse and because their technology has long been worked out, they are quite widely used, even at the present time.

Sometimes, examples of economy comparison calculations are given for solid and

liquid propellants. The cost of 1 kg of rocket weight is determined by the equation

$$K_R = \xi K_p + (1 - \xi) K_N$$

where:  $K_p$  = the cost of 1 kg of fuel,

$K_N$  = the cost of 1 kg of rocket construction without fuel,

$\xi$  = the fuel coefficient =  $W_p/W_R$

in which:  $W_p$  = the weight of the fuel;  $W_R$  = the initial weight of the entire rocket without payload (nose cone).

Ernest R. Roberts gives the maximum costs [10] for solid fuels

$K_N$  = \$44.00 per kilogram,

$K_p$  = \$ 2.20 per kilogram,

$\xi$  = 0.9

Accordingly, when  $I_s = 245$  sec, the cost per kilogram of initial rocket weight is \$6.38. The cost of 1 kilogram of initial weight of liquid fuel rockets (due to the high cost of  $K_N$ , which is \$200.00, and the large  $\xi$  coefficient) averages \$13.00, even for the least expensive fuels. Therefore, even when we assume that a solid fuel rocket is 1.5 times heavier than a liquid fuel rocket, its cost will be about 27% less. Attention must still be given to the most suitable conditions of stockpiling, use and comparative dependability of function, which speak for the advantages of solid propellants.

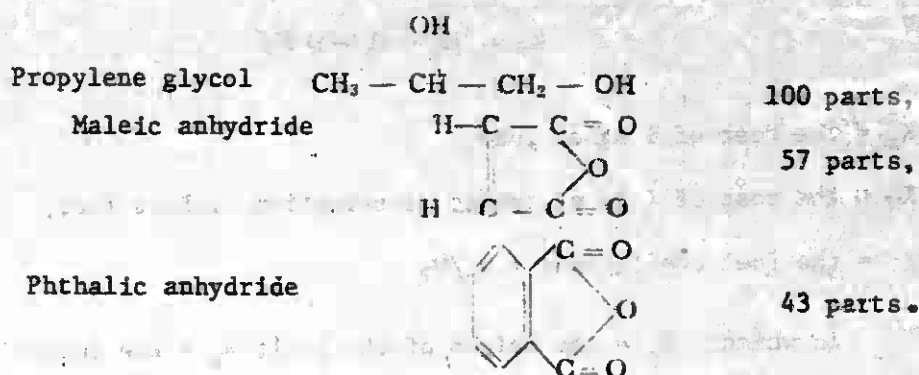
#### 1.4.1. An example of the computation of the theoretical specific impulse for a composite rocket propellant.

##### Determination of the empirical equation of the organic portion of the propellant

By means of example, we take a propellant of the composite type, in which polyester resins are used as the combustible substance and the binder, and potassium perchlorate as the oxidizer.

The polyester resin (designated as "Polimal 110") is a mixture of polyester (55%) and styrene (45%). The polyester is obtained by condensation of the following

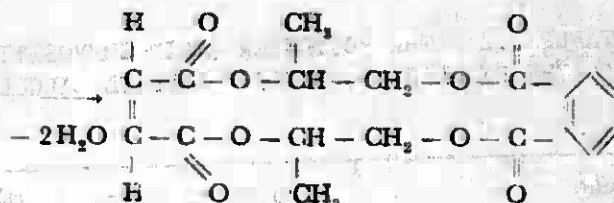
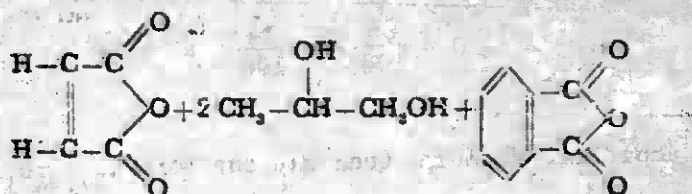
Components:



It is evident that the component which is capable of facilitating polymerization is maleic anhydride; because of it, the resin is capable of polymerization. Copolymerization of the condensate with styrene takes place in the presence of styrene; this is the so-called hardening of the resin. One mole of glycol enters the condensate for each mole of anhydride. In technological data, resins are usually given the molecular weight attributed to one double bond and the molecular weight of the mer (the mean weight of the glycol-acid composition). It follows from these technological data that all the acid and alcohol groups are esterified. A glance at Table 1.2 will confirm this.

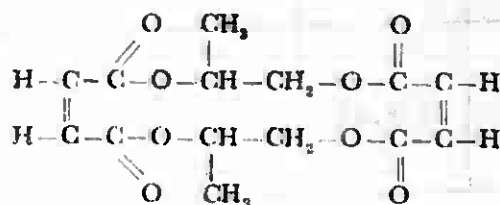
The summary product of the molecular weight and the number of moles divided by 100 (the number of glycol-acid moles) should give the weight of the mer in moles. We obtain 195.76 by the division. The molar weight of the mer is given as 177.7, that is, the above minus the molar weight of water.

It follows from this that a complete condensation, together with groups in the end of the chain, has taken place in the mixture. On the basis of the data, a schematic (in agreement with the numerical data) condensation structure can be established. Because the phthalic anhydride is less than maleic, it follows that 86% of the condensate (twice the phthalic anhydride fraction) arose from the combination of two glycols and two different anhydrides



The empirical formula of the product =  $\text{C}_{18}\text{H}_{18}\text{O}_8$ .

The remaining 14% of the condensate arises from the glycol and maleic anhydride. The simplest form of this product is the condensation of two glycol molecules with two anhydride molecules.



The empirical formula =  $\text{C}_{14}\text{H}_{16}\text{O}_8$ .

For all practical purposes, the condensation product ring formation of this type may be much greater, but the summary formula will be reduced to the cited simplest form.

The mean summary formula is calculated from these two summary formulas, taking into account the percent participation of each of these. The following numbers of atoms will be found in this final formula:

$$\text{C} = \frac{86}{100} 18 + \frac{14}{100} 14 = 17.44$$

$$\text{H} = \frac{86}{100} 18 + \frac{14}{100} 16 = 17.72$$

$$O = \frac{86}{100} 8 + \frac{14}{100} 8 = 8.00$$

The mean empirical formula then has the form  $C_{17.44}H_{17.72}O_8$ , and its molecular weight is 355.

TABLE 1.2. THE POLYESTER RESIN COMPOSITION USED IN THE EXAMPLE OF SPECIFIC INPUT CALCULATIONS

Condensate composition	mol. wt.	Amount in parts by weight in the condensate	The product of the mol. wt. and the number of moles
$\begin{array}{c} \text{OH} \\   \\ \text{CH}_2 - \text{CH} - \text{CH}_2\text{OH} \end{array}$	76.09	100	7609
$\begin{array}{c} \text{H} - \text{C} - \text{C} - \text{O} \\    \quad \diagup \quad   \\ \text{H} - \text{C} - \text{C} - \text{O} \end{array}$	98.06	57	5589
$\begin{array}{c} \text{C} - \text{O} \\   \quad \diagup \\ \text{C} - \text{O} \end{array}$	148.11	43	6369
—	—	—	total 19576

Assuming in accordance with the given composition that 355 g is 55% of the resin composition, we calculate the amount of styrene, in grams, devolving upon this amount of condensate

$$\frac{45}{55} \cdot 355 = 291$$

The simplified summary CH styrene formula has a molecular weight of 13. Accordingly, the subscript of CH, as occurring in the calculated amount, is  $291 : 13 = 22.38$ .

By summing, we obtain:

Empirical formula of the condensate	$C_{17.44}H_{17.72}O_8$ (mol. wt. 355)
Empirical formula of the styrene	$C_{22.38}H_{22.38}$ (mol. wt. 291)
General empirical formula of the binder	$C_{39.82}H_{40.10}O_8$ (mol. wt. 646)

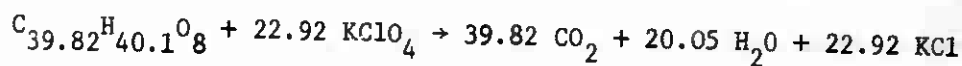
#### Determination of the required percent composition of the fuel

Proceeding to the designing of a composite fuel, primary consideration must be given to establishing the required binder-oxidizer ratio. For this purpose it is necessary above all to know the oxidizer decomposition equation.

The equation for the decomposition of potassium perchlorate has the form



Fuel combustion can be complete and incomplete. In the case of complete combustion (C to  $CO_2$  and H to  $H_2O$ ), the percent composition of the fuel is in accordance with the formula



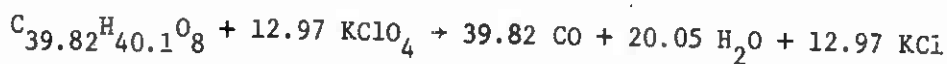
$$\text{mol. wt. } 646 + 22.92 \cdot 138.55 = 646 + 3175 = 3821$$

$$3821 - 100\%$$

$$X = \frac{646 - X}{3821} = 16.9\% \text{ binder}$$

$$83.1\% KClO_4$$

For incomplete combustion but complete gasification\* (C to CO and H to  $H_2O$ ), we calculate the percent composition according to the scheme



$$\text{mol. wt. } 646 + 12.97 \cdot 138.55 = 646 + 1797 = 2443$$

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\*Translator's note: for want of a better word...



$$2443 - 100\%$$

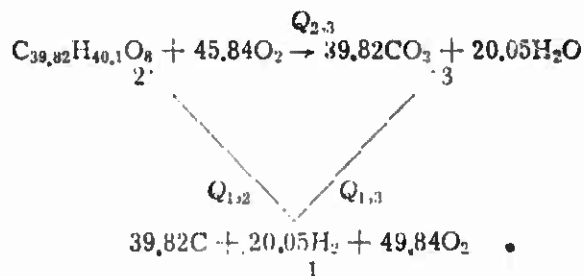
$$X = \frac{646 - X}{2443} = 26.4\% \text{ binder}$$

$$73.6\% \text{ KClO}_4$$

Not every composition that is determined and substantiated in a purely theoretical manner can technically be prepared. Of the two compositions calculated above, the first is more advantageous from an energy point of view; the second, however, although it is not quite as good with respect to energy, is technically much easier to prepare. Therefore, propellants of this type are always brought closer to the composition of the second, which is also the basis for further calculations, cited below, leading to the determination of the specific impulse.

#### Determination of the enthalpy of the substrates

In order to calculate the specific impulse for a given propellant according to formula (1.25), the combustion temperature and the exact decomposition formula must be known. A knowledge of the thermal effect of the decomposition reaction, which results from a knowledge of the enthalpy of the substrates and products, is necessary in order to calculate the temperature and composition of the combustion gases. The enthalpy of the resins and various polymers is usually denoted by the given heat of combustion (if the heat of combustion is not given in the literature, it must be calculated by calorimetric methods). The calculated heat of combustion for the considered resin is 7110 kcal/kg. The enthalpy is calculated on the basis of Hess' law according to the scheme



where:  $Q_{2,3}$  = the heat of combustion of the resin (measured);

$Q_{1,3}$  = the heat of formation of the products (calculated),

$Q_{1,2}$  = the sought heat of formation of the resin.

$$Q_{2,3} = 7110 \text{ kcal/kg} = \frac{646 \cdot 7110}{1000} = 4593 \text{ kcal/mole}$$

$$Q_{1,3} = 39.82 \Delta H_{\text{CO}_2}^0 + 20.05 \Delta H_{\text{H}_2\text{O}_c}^0 = 39.82 \cdot 94 + 20.05 \cdot 68.3 = 5108 \text{ kcal}$$

where:  $\Delta H_{\text{CO}_2}^0$  = the normal enthalpy of carbon dioxide,

$\Delta H_{\text{H}_2\text{O}_c}^0$  = the normal enthalpy of water as a liquid.

From Hess' law

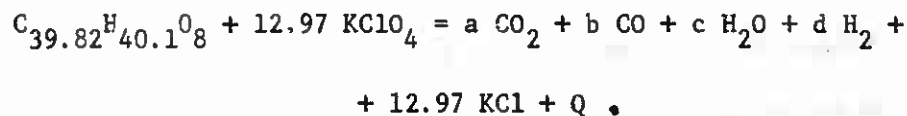
$$Q_{1,3} = Q_{1,2} + Q_{2,3}$$

$$Q_{1,2} = Q_{1,3} - Q_{2,3} = 5108 - 4593 = 515 \text{ kcal/mole}.$$

The heat of formation of  $\text{KClO}_4$  is 12.7 kcal/mole<sup>2)</sup>.

Calculation of the combustion temperature and the composition of the combustion gases

For the considered composition (incomplete combustion) the decomposition equation is composed of several unknown coefficients:



Calculation of the temperature and composition of the combustion gases is specifically limited to finding these coefficients.

We set up the following set of equations:

$$(1) \quad a + b = 39.82 \quad \text{total carbons;}$$

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<sup>2</sup>See page 86.

- (2)  $2c + 2d = 40.1$  total hydrogens;  
 (3)  $2a + b + c = 4 \cdot 12.97 + 8$  total oxygens;  
 (4)  $a + b + c + d + 12.97 = n$  total of all molecules;

(5)  $K_{wg} = \frac{p_{CO} \cdot p_{H_2O}}{p_{CO_2} \cdot p_{H_2}} = \frac{b \cdot c \cdot 70}{a \cdot d \cdot n}$  the equilibrium of water gas;  
 $CO_2 + H_2 \rightleftharpoons CO + H_2O$  at a  
 pressure of 70 atm.

The cited set of equations is the simplest set used in this type of calculations. Nevertheless, in a concrete case, when the amount of oxygen in the propellant composition is not sufficient for complete combustion ( $CO_2$  and  $H_2O$ ) and when it is known that the combustion temperature is not too high, the simplification used is sufficiently accurate.

In other cases, when there is a sufficient amount of oxygen in the fuel, the carbon dioxide dissociation constant and the water dissociation constant must be considered separately instead of the equilibrium constant of water gas.

$$K_{CO_2} = \frac{p_{CO}^2 \cdot p_{O_2}}{p_{CO_2}^2} = \frac{b^2 \cdot e \cdot 70}{c^2 n}$$

$$K_{H_2O} = \frac{p_{H_2} \cdot p_{O_2}}{p_{H_2O}^2} = \frac{d^2 \cdot e \cdot 70}{c^2 \cdot n}$$

In this manner we have one equation and one unknown (with  $O_2$  coefficient  $e$ ) more; then the method of solving the set remains the same. In the case of higher temperatures (above  $2500^\circ K$ ), it is likewise absolutely necessary to take into account the molecule-to-atom dissociation, whereby we are obliged to deal with a larger number of unknowns and a larger number of equations. Then the resolution system also remains the same except that, obviously, the resolution of a set containing a larger number of equations requires more work<sup>3</sup>.

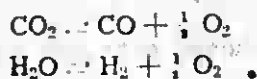
<sup>3</sup>See page 86.

In our case, where we have a fuel with a relatively small calorific value and an insufficient amount of oxygen, we employ only the equilibrium constant of water gas in addition to the material equilibrium equations.

The water gas equilibrium equation has the form



By its nature it is a sum of the dissociation equations of  $\text{CO}_2$  and  $\text{H}_2\text{O}$



When there is an oxygen deficiency in the fuel, the oxygen evolving in the  $\text{CO}_2$  dissociation can oxidize the hydrogen evolving during the dissociation of water vapor and inversely, the oxygen from the  $\text{H}_2\text{O}$  can oxidize the CO.

In this manner the set of five equations will be solved if we assume some value of  $K_{\text{wg}}$ .

We assume that  $T = 1800^\circ\text{K}$ , and  $K_{\text{wg}} = 3.967$  [14].

In the first four material equilibrium equations it is convenient to designate the unknowns in terms of one unknown, for example  $d$ :

$$\begin{aligned}c &= 20.05 - d \\ b &= 39.82 - d \quad a = d \\ n &= 72.84.\end{aligned}$$

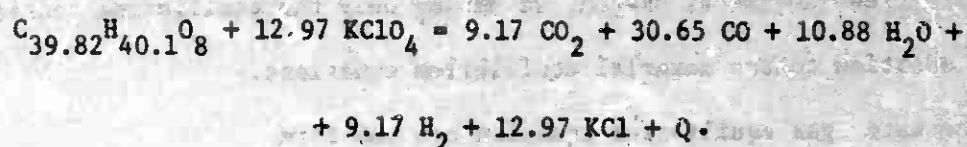
On the basis of these values for the water gas equilibrium equation, we calculate  $d$

$$\frac{b \cdot c \cdot 70}{a \cdot d \cdot n} = \frac{(39.82 - d)(20.05 - d) \cdot 70}{d \cdot d \cdot 72.84} = 3.967.$$

After resolution, we obtain  $d = 9.17$ , thus

$$\begin{aligned}a &= 9.17 \\ b &= 39.82 - 9.17 = 30.65 \\ c &= 20.05 - 9.17 = 10.88 \\ n &= 72.84.\end{aligned}$$

Accordingly, the decomposition equation in the first approximation has the form



The results of the first approximation calculations are verified by comparing the product and substrate enthalpies, which should be equal if the initial temperature assumptions are correct.

Normal enthalpy and standard enthalpy are synonyms of this same concept, which is sometimes called "enthalpy" for short and which must not be confused with the absolute enthalpy. The heat of formation is the standard enthalpy of bonding under normal, that is, standard (25°C; 1 atm) conditions.

The heat of formation of the substrates is comprised of

the heat of formation of the resin 515 kcal

the heat of formation of  $\text{KClO}_4$   $12.97 \cdot 112.7 = 1460$  kcal

A total of 1975 kcal .

The standard enthalpy of the combustion products is constituted by the sum of the enthalpies of the individual products under combustion conditions.

The tables of thermodynamic constants do not give the enthalpy of KCl at high temperatures; accordingly, it is calculated by summing

the heat of formation of KCl 104.3

the heat of heating solid KCl  $(1093 - 298)0.013 = -10.4$

the heat of fusion of KCl - 6.4

the heating of liquid KCl  $(1680 - 1093)0.0165 = -9.6$

the heat of vaporization of KCl - 38.84

the heating of gaseous KCl  $(1800 - 1680)0.009 = -1.1$  .

The total enthalpy of KCl is 38 kcal/mole.

In the cited case, the enthalpy of the products is comprised of the enthalpies

KCl	1297.38	=	492
CO <sub>2</sub>	9.17 · 74.99	=	687
CO	30.65 · 14.55	=	447
H <sub>2</sub> O	10.88 · 42.81	=	466
H <sub>2</sub>	9.17 · (-11.07)	=	-101

Total 1991 kcal.

The difference between the product and substrate enthalpies is 1991 - 1975 = 16 kcal.

A difference in the enthalpies up to 20 kcal is permissible; accordingly, the data of the first approximation can be assumed to be correct.

#### Calculation of the specific impulses

Having an accurate decomposition equation, the mean molecular weight of the combustion products  $M$  can be calculated and, for the purpose of calculating the mean adiabatic exponent  $k$ , the mean molar heat under constant pressure  $C_p$  and at a constant volume  $C_v$ .

The mean molecular weight of the combustion products is:

$$M = \frac{m}{n} = \frac{2443}{72.84} = 33.55$$

where:  $m$  = the weight in grams of the considered amount of burned propellant (in our case, it is

$$\text{mol. wt. } C_{39.82}H_{40.1}O_8 + 12.97 \text{ KClO}_4 = 2443),$$

$n$  = the sum of the evolved moles of gas.

The values  $C_p$  and  $C_v$  for 1800°K are calculated from the equations given in the tables for the individual gases<sup>4</sup>.

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<sup>4</sup>See page 86.



$$\begin{aligned}
C_{p, \text{co}} &= 7.7 + 5.3 \cdot 10^{-3} \cdot 1800 - 0.63 \cdot 10^{-6} \cdot 1800^2 = 14.48 \\
C_{p, \text{cu}} &= 8.8 + 1.2 \cdot 10^{-3} \cdot 1800 = 8.78 \\
C_{p, \text{H}_2\text{O}} &= 7.2 + 2.7 \cdot 10^{-3} \cdot 1800 = 12.07 \\
C_{p, \text{H}_2} &= 8.82 + 0.81 \cdot 10^{-3} \cdot 1800 = 8.08 \\
C_{p, \text{KCl}} &= \text{approximate value [15]} = 9.0
\end{aligned}$$

$$C_{p, \text{mean}} = \frac{\sum \text{mol} \cdot C_p}{n} = \frac{9.17 \cdot 14.46 + 30.65 \cdot 8.76 + 10.80 \cdot 12.07 + 9.17 \cdot 8.08 + 9 \cdot 12.97}{72.84}$$

$$C_{p, \text{mean}} = 10.07 \quad C_v = 10.0700 - 1.9872 = 8.0828$$

$$h = \frac{C_p}{C_v} = \frac{10.0700}{8.0828} = 1.246$$

By substituting all the data into the equation (1.25), we obtain:

$$I_s = \sqrt{\frac{2 \cdot 1.246}{9.81 (1.246 - 1)} \frac{(427 \cdot 1.9872) \cdot 1800}{33.55} \left[ 1 - \left( \frac{1}{70} \right)^{\frac{1.246 - 1}{1.246}} \right]}$$

After carrying out the computations,

$$I_s = 164.7 \text{ sec.}$$

Similar compositions tested in practice furnish an impulse close to the above value, whereby it can be greater with combustion under higher pressure. The maximum  $I_s$  for propellants of this type is attained at a pressure of about 85 atm.

#### 1.4.2. Treatment of the results of experimental investigations

Studies on solid propellants are usually carried out in chambers with a nozzle measuring the force of thrust and pressure in time. The apparatus for these measurements is comprised of the following basic parts: combustion chamber, gauges to gather and record the measured parameters and a recording apparatus. The combustion chamber may be in a horizontal or vertical position during the measuring. In addition to the nozzle, a chamber of this type should have openings for the pressure gauges (one at the bottom and one at the nozzle) and pressure relief valves, which open when there is an unexpected, excessively violent pressure increase. The

gauges can be quite divergent; most frequently, however, the gauges used are those which induce an electric impulse, i.e., induction, piezoelectric, capacitative (condenser-type), tensometric and others. The mechanical and optical gauges constitute another type. The registering apparatus in the case of gauges producing electric impulses is usually a multiloop oscilloscope.

For example, a charge in the shape of a tube, with dimensions:  $D = 41 \text{ mm}$ ,  $d = 8 \text{ mm}$  and  $l = 128$ , and with a weight of 300 g, is burned. Chamber dimensions: internal diameter = 44.5 mm, length = 162 mm, and the critical diameter of the nozzle, 10.3 mm. A pyrotechnic primer (5 g) with an electric igniter is used. The time, pressure and thrust is measured. Figures 1.6 and 1.7 illustrate the pressure and thrust curves.

The combustion time, the average and maximum combustion pressure and the average and maximum thrust are evident from these data. From this combustion curve we can calculate the total impulse, specific impulse and burning rate and it is possible to determine the numerical dependency of the burning rate on the pressure and temperature at various pressures and temperatures. The combustion time resulting from the curve at the known scale of the registering apparatus is about 0.42 seconds. We calculate the mean combustion pressure with the equation

$$P_{av} = \frac{\int_0^t p dt}{t}$$

In our case, the surface area under the  $p(t)$  curve in Figure 1.6 is<sup>5</sup> 1680 mm<sup>2</sup> and the pressure scale, 4.75 kg/cm<sup>2</sup>. The time scale is 0.2 : 37 = 0.0054 sec/mm. By substituting these data in the above equation, we obtain

$$P_{av} = \frac{1680 \cdot 4.75 \cdot 0.0054}{0.42} = 102.3 \text{ kg/cm}^2.$$

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<sup>5</sup>See page 86.

The maximum combustion pressure results directly from the curve and customary scale:  $4.75 \cdot 35 = 166 \text{ kg/cm}^2$ .

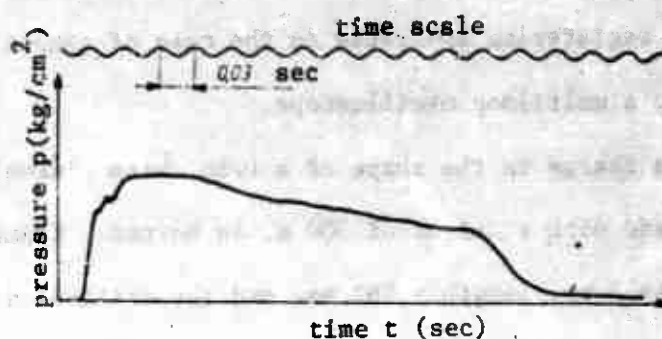


Figure 1.6. Pressure curve over time, registered on an oscilloscope during combustion

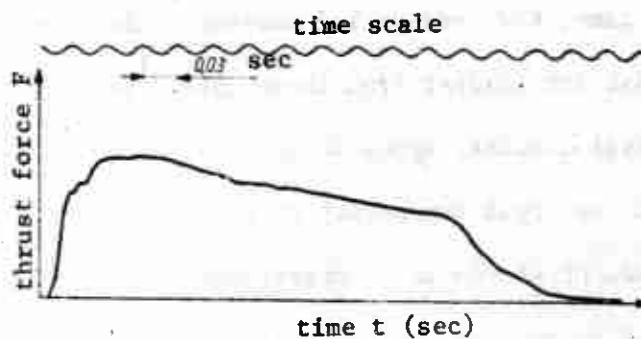


Figure 1.7. Thrust curve over time, registered on an oscilloscope during combustion

Similarly, the average and maximum thrust is calculated from the thrust curve

$$F_{av} = \frac{\int_0^t F \cdot dt}{t} = \frac{I}{t} \cdot$$

which is the total impulse divided by time

$$I = \int_0^t F \cdot dt = 2180 \quad \cdot \quad 43 \quad \cdot \quad 0.0054 = 50.6 \text{ kg} \cdot \text{sec}$$

surface area  
under curve  
 $\text{m}^2$

scale of  
thrust force  
 $\text{kg/mm}$

time  
scale  
 $\text{sec/mm}$

$$F_{av} = \frac{I}{t} = \frac{50.6}{0.42} = 120.5 \text{ kg}$$

$$F_{max} = 4.3 \cdot 37 = 159.1 \text{ kg}$$

$$\text{The specific impulse } I_s = \frac{I}{m} = \frac{50.6 \text{ kg} \cdot \text{sec}}{0.3 \text{ kg}} = 168.7 \text{ sec}$$

The burning rate results from the thickness of the combustion layer and time.

In our case

$$r = \frac{41 - 8}{4 \cdot 0.42} = 19.6 \text{ mm/sec} = 1.96 \text{ cm/sec}$$

### 1.5. Erosive Combustion

The considered burning rate dependencies on the basic parameters (pressure and initial temperature) refer to the frontal combustion. In the burning of charges having such a form that a gas stream flows parallel to the combustion walls, the burning rate is a function of other factors also. One of these is the speed of the flowing gases. In the case of erosive combustion, there are, of course, various mathematical approaches, but all are based on a similar interpretation of the mechanism of the effect. In order to support combustion, the surface of the propellant must receive heat, by means of which its temperature is raised to the temperature of ignition. At the surface of the propellant the heat traverses the initial gasification zone, in which the first combustion stage occurs.

The gasification zone is a few hundredths of a millimeter thick [17] and is sometimes called the transition stage or zone [18]. The heat of the flame zone, in which the main combustion process occurs, passes through this zone. The linear burning rate of the propellant is a function of the amount of heat furnished. The heat passing through the transition zone is supplied by conduction, radiation and convection.

When there is a parallel flow of gases along the combustion surface, thermal

conduction begins to assume a greater significance by convection. Heat convection is proportional to the speed of the flowing gases. This speed increases over the length of the fuel charge from the front side to the nozzle discharge. Hence, the combustion erosivity increases along the charge, beginning from the bottom section of the chamber to the discharge section. It is well to first consider the experimental methods of determining the erosive combustion and then to proceed to the mathematical approach to the problem. Experimental methods of erosion determination are quite divergent, as are the mathematical methods of solving this problem. All theoretical calculation methods yield results that are more or less in agreement with the experimental results. The difficulties involved in the equivalent theoretical approach and in the treatment of universal experimental methods arise from the fact that the burning rate is simultaneously dependent on a great many factors which act mutually and cannot be considered individually to the exclusion of the others. These factors are, e.g., pressure, initial charge temperature, flame temperature during combustion, heat of explosion, combustion product composition, the velocity of the gases flowing parallel to the burning surface, etc.

#### 1.5.1. Experimental study of erosive combustion

Double combustion chambers are used in the experiments. In one portion of the chamber only gases causing erosion are formed; in the other, specifically, in the tube connected with the first chamber, are found the samples studied. The pressure in such an engine and the gas discharge were varied by varying the critical cross sectional area of the nozzle and the size of the grain producing the gas streams. The propellant samples studied had the form of short cylinders burning on the inside, tablets, bars and inserts in the form of the nozzle. Composite fuels were investigated (Table 1.3). It is evident from the Table that propellants containing varying amounts of oxidizing substances, thus having varying energy contents, were studied. In this manner it was possible to study the erosion at different combustion temperatures. Interpretation of the results is made more difficult, however,

because together with the energy content of the fuel, the molecular weight of its combustion products, the thermal conduction of the fuel, the burning rate without erosion, etc. are changed. In connection with this, it is quite difficult to determine which of these factors is decisive in varying the magnitude of erosive combustion. Nevertheless, the results obtained are quite interesting and are comparable to those obtained with many other methods of experimentation. This substantiates the validity of the chosen method.

X-rays are used in studying the changes in grain dimension in time. The diagram of the chamber and the apparatus for measuring the changes in size of the studied charge is given in Figure 1.8. In a separate engine the basic charge after ignition produces the gas stream which flows through the cylinder of propellant studied. After a definite, arbitrarily chosen period of time, an x-ray of the studied cylinder is made. In this manner the specific increase in the internal diameter of the cylinder during a definite period of time is obtained. From this we obtain the burning rate.

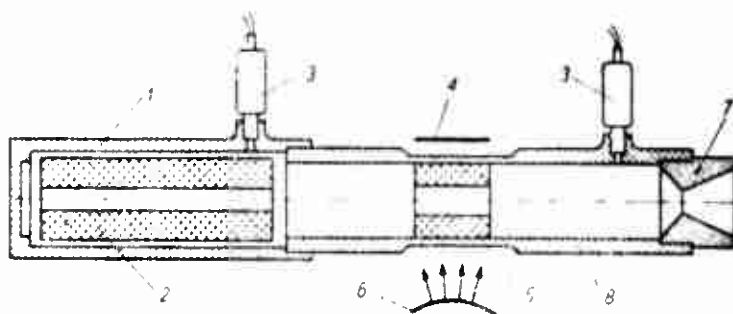


Figure 1.8. Chamber for studying erosive combustion. Key: 1 = engine; 2 = basic charge; 3 = pressure gauge; 4 = photographic film; 5 = the studied cylindrical charge; 6 = x-ray source; 7 = nozzle; 8 = steel cylinder.

When the average pressure in the considered period of time and the burning rate of the propellant without erosion under this pressure are known, it is possible to determine the erosive combustion rate.

The burning rate of the fuel without erosion is determined in the so-called



TABLE 1.3. A COMPARISON OF PROPELLANTS AND THEIR PARAMETERS SUBJECTED TO A STUDY OF EROSION COMBUSTION

Fuel	Components	Oxidizer		Binder [wt. %]	$\rho$ [g/cm <sup>3</sup> ]	Combustion products			Speed of sound [m/sec]
		%	average dimensions of particles [ $\mu$ ]			t [°C]	mean mol. wt.	output coefficient [10 <sup>-4</sup> sec/m]	
A	NH <sub>4</sub> ClO <sub>4</sub> + polyester	65	24-30	35	1.62	1690	21	8.6	930
B	NH <sub>4</sub> ClO <sub>4</sub> + polysulfide + epoxy resin	65	24-30	35	1.63	1750	22	8.5	940
C	NH <sub>4</sub> ClO <sub>4</sub> + polysulfide + epoxy resin	75	24-30	25	1.70	2550	25	7.5	1020
D	NH <sub>4</sub> ClO <sub>4</sub> plus KClO <sub>4</sub> (3:1) + polysulfide + epoxy resin	70	24-30 KClO <sub>4</sub> -20	30	1.74	2220	26	8.2	940

Crawford bomb (Figure 2.1). The determination here is based on the determination of the burning rate of the bar of fuel which is burning only on the front surface.

In the testing arrangement for erosive combustion, a small window of quartz sheets, to which a tablet of fuel is made to adhere, can be used instead of x-rays. After burning the tablet (having a known thickness at a known mean pressure), an emitted light signal indicating the end of combustion is registered by a photocell. When the ignition time and the time the burning is complete are known, we have the burning time, which permits the calculation of the mean total burning rate and from this we can calculate the erosive burning rate

$$r_e = r - r_p \quad (1.27)$$

The results of the summary measurements of the burning rate of the tablets at various gas temperatures are given in Table 1.4. It is evident from the table that the temperature of the gases in the stream can be varied from 1690°K to 2550°K in

TABLE 1.4. THE RESULTS OF MEASURING THE TOTAL BURNING RATE IN EROSIVE COMBUSTION STUDIES

Propellant	Conditions in engine		Absolute burning rate [cm/sec]		Frontal burning rate $r_p$ [cm/sec]
	gas velocity [m/sec]	pressure [atm]	basic charge with A $T_f = 1690^\circ\text{K}$	basic charge with C $T_f = 2550^\circ\text{K}$	
A	50	20	$0.29 \pm 0.01$	$0.30 \pm 0.01$	0.26
	50	100	$0.75 \pm 0.05$	$0.72 \pm 0.01$	0.47
	100	20	$0.38 \pm 0.02$	$0.39 \pm 0.02$	0.26
	100	100	$1.03 \pm 0.06$	$1.02 \pm 0.04$	0.47
B	500	100	$0.90 \pm 0.04$	$0.95 \pm 0.01$	0.85
	100	100	$1.20 \pm 0.02$	$1.19 \pm 0.03$	0.85
	225	20	$0.60 \pm 0.02$	$0.63 \pm 0.02$	0.51

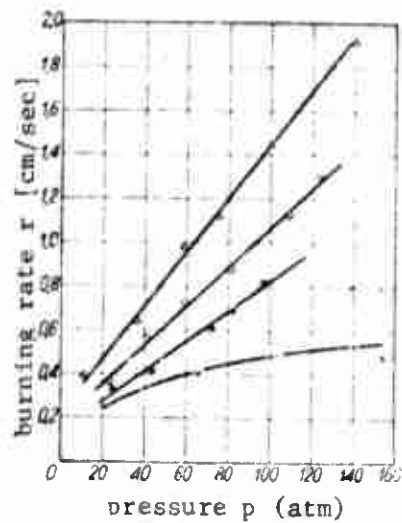
this arrangement without changing the propellant studied. The cited results show that a pressure variation has the greatest influence on the burning rate, the rate of gas flow has a lesser effect and the temperature of the flowing gases has the least influence. The influence of the temperature is so slight that with a difference of  $860^{\circ}$  the difference in the burning rate very probably remains within the limits of measurement error. The fact that in 7 combustion tests, a lesser burning rate was observed at higher temperatures in 2 cases serves to confirm this.

The burning time of the studied sample can also be determined by means of the pressure indicator. There is an opening leading to the pressure gauge at the site of adhesion of the studied tablet to the cylinder wall. When combustion is complete, the opening opens and the pressure impulse is transmitted to the gauge, which records the time of completion of the combustion. In order to study the erosivity of long charges, the tests are carried out with the propellant bars affixed to the cylinder, as with the tablets. The burning rate was studied at 2 points: at the beginning and at the end of the band. After calculation, it turned out that for a length of about 7 cm the rate of erosive combustion  $r_e$  was 20-30% greater at the beginning than at the end. The results of the experiments performed are shown in the graphs in Figures 1.9 and 1.10.

It is evident from the graphs that propellant C is only slightly subject to erosion at low pressures. It is interesting to note that the value of the total burning rate under high pressure is of the same order for different fuels, although their heats of combustion and frontal burning rates are quite divergent.

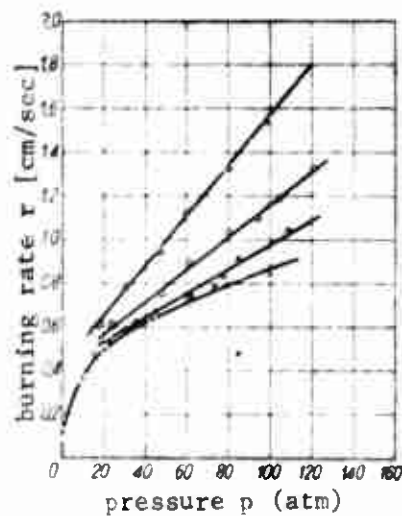
Hence it is deduced that the  $r_e$  value is lower for propellants with a higher burning rate without erosion  $r_0$ . As shown in the graphs, there is one definite boundary rate which is also a function of the velocity of the gas stream for such divergent fuels as these.

In order to study erosive combustion at gas velocities equal to the speed of sound, fuel inserts are used in the critical cross sections of the nozzle. The constancy of the nozzle cross section was regulated by a metallic encasement of the



x frontal combustion  
 ● erosive combustion gas velocity 49 m/sec  
 ○ " " " " 103 m/sec  
 Δ " " " " 204 m/sec

Figure 1.9. Erosive combustion of propellant A.



x frontal combustion  
 ● erosive combustion gas velocity 49 m/sec  
 ○ " " " " 103 m/sec  
 Δ " " " " 204 m/sec

Figure 1.10. Erosive combustion of propellant C.

nozzle. The rate of erosive combustion under these conditions was of the same order as with flat samples. However, in this case the streams of circumfluent gases were considerably different than the preceding ones and the temperature of the gases was considerably lower because of expansion. Here the deduction of the slight effect of temperature on the rate of erosive combustion was confirmed and it is assumed that the gas velocity has a definite boundary value, above which the rate of erosive combustion does not increase with increasing rate of flow.

Erosion is also frequently determined by stopping the burning of the charge after a definite period of time. For an experimentation of this type a rather long charge is taken and placed in a chamber similar to an ordinary rocket engine, but with an arrangement which makes it possible to open the chamber and eject the charge at any given moment. The extinguished charge has a different thickness of burned layer over its entire length -- a minimum thickness in the front portion and a maximum thickness in the back. In addition, a chamber of this type has gauges for measuring the pressure. The gas velocity for each point on the entire length is calculated theoretically. Thus, it is possible to obtain all the data for calculating the rate of erosive combustion as a function of the rate of gas flow and the pressure in the combustion chamber. A defect in this method is the inability to change the temperature of the stream without changing the studied charge. Therefore, if we wish to take the temperature factor into consideration, the best we can do is study the combustion of the thermostatic charges beforehand at various temperatures. Nevertheless, this can not be taken to be equivalent to the temperature variation of the gas stream, because in this case the temperature of the stream changes due to heat furnished to the fuel in order to bring it to normal temperature, but at the same time the thermal conduction of the propellant, the temperature of the gases evolving in the studied portion, the conduction of the laminar layer, etc. are changed.

### 1.5.2. Mathematical treatment of erosive combustion

In experimental works the following equation is often used for the burning rate with erosion

$$r = a p^n + C v a p^n \quad (1.28)$$

where:  $v$  = velocity of the flowing gases;

$C$  = a constant determined on the basis of analysis of the results of many interrupted combustion experiments.

Nevertheless, this equation is not precise and requires a great deal of experimental data on interrupted combustion. There are many variations of the equation in this form.

For example, C. Huggett [19] offers

$$r = r_p (1 + K \rho_g v) \quad (1.29)$$

where:  $\rho_g$  = the density of the flowing gases;

$K$  = the constant characteristic for the given propellant.

In other works [13 and 20] the following equation is offered

$$\frac{r}{r_p} = 1 + K_a \frac{V}{a_f} \quad (1.30)$$

where:  $a_f$  = the speed of sound in the combustion products at flame temperature  $T_f$ ;

$K_a$  = the constant characteristic for the given propellant, or

$$\frac{r}{r_p} = 1 + K_m \frac{m}{m^*} \quad (1.31)$$

where:  $m$  = the mass velocity  $\text{g/cm}^2 \cdot \text{sec}$ ;

$m^*$  = the critical mass velocity when  $M = 1$  ( $M$  = Mach number).

However, none of these equations furnished satisfactory results when compared with experimental data.



Derivation of a suitable equation is based on the a priori assumption of the general equation:

$$r = r_p + r_e \quad (1.32)$$

where:  $r$  = the summary burning rate,

$r_p$  = the rate of combustion without erosion (a function only of the pressure  $p$ ),

$r_e$  = the erosive rate of combustion.

The following procedure is employed to derive the special equation:

The central stream of combustion gases is enveloped by the so-called primary combustion zone, also called the gasification zone (the zone is a few hundredths of a millimeter in thickness), and this in turn is surrounded by the fuel zone. The gasified propellant is continuously diffusing from the fuel to the gas stream. These gases enter the stream at right angles to the direction of motion of the stream and with a mass velocity equal to the product of the burning rate and the fuel density. The influence of the stream velocity on the burning rate depends on facilitation of the heat exchange from the flame to the propellant surface and on the influence of friction itself in the mechanical sense. Because friction and heat conduction are both functions of these same parameters of the flowing gases, only the heat conduction is considered here in the simplification. This conduction as well as the friction between the stream and the surface are reduced by gas diffusion from the surface of the fuel. The diffusing gases act as a lubricant by reducing the friction of the gas stream on the walls of the fuel. The relationship of the coefficient of heat conduction with diffusion  $\underline{h}$  to heat conduction without diffusion  $\underline{h}_0$  is expressed by the equation

$$\underline{h} = \underline{h}_0 e^{-\beta \delta} \quad (1.33)$$

where:  $\beta$  = the uniform experimental constant;

$Q$  = the mass velocity of the diffusing gas;

$G$  = the mass velocity of the combustion products.

The erosive rate of combustion is proportional to the heat conduction coefficient. Accordingly, by substituting (1.33) into (1.32) in the developed form, we obtain

$$r = ap^n + Kh_0 e^{-\beta Q/G} \quad (1.34)$$

where  $K$  = the coefficient of proportionality.

The coefficient of heat conduction without diffusion (with the stream flow over the stationary plane) is calculated from the empirical equation

$$h_0 = 0.0288 G c_p Re^{-0.2} Pr^{-0.467} \quad (1.35)$$

where:  $c_p$  = the specific heat of the combustion products under constant pressure,

$Re$  = the Reynolds number reckoned from the beginning of the stream<sup>6</sup>,

$Pr$  = the Prandtl number<sup>7</sup>.

After substituting (1.35) in (1.34), we obtain

$$r = ap^n + K \cdot 0.0288 G c_p Re^{-0.2} \cdot Pr^{0.467} e^{-\beta Q/G} \quad (1.36)$$

After substituting the expression  $Re = GL/\mu g$  for the Reynolds number and by designating the power exponent  $\beta Q/G$  by  $z$ , we obtain

$$r = ap^n + (0.0288 c_p \mu^{0.2} \cdot Pr^{0.467}) K \frac{G^{0.8}}{L^{0.2}} e^{-\beta Q/G} \quad (1.37)$$

where  $L$  = the length measured from the front portion of the grain.

The combustion products of many solid propellants have approximate viscosities, Prandtl numbers and specific heats. Therefore, we denote the expression in parentheses with  $K$  by one symbol

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<sup>6,7</sup> See page 86.

$$\alpha = (0.0288 c_p \rho_c^{0.2} \cdot Pr^{0.667})^{1/2} \quad (1.38)$$

As a result, equation (1.37) has the form

$$r = c p^n + \frac{G^{0.8}}{L^{0.2} e^{\alpha}} \quad (1.39)$$

As a result of the lubricating action of the diffusing gases, when the burning rate is high,  $z$  is large (in connection with the large  $Q$  value); then the erosive combustion for fast-burning fuels is insignificant, which is in agreement with experimental data.

The constants  $\alpha$  and  $\beta$  (in the expression for  $z$ ) are calculated by the method of tests and comparisons with experimental data obtained by measuring the velocity of combustion products in the critical cross section of the nozzle. However, this method is very laborious and the calculations can be performed only with the aid of computers because of the large number of variables.

The coefficient  $a$  can also be calculated theoretically, beginning with the heat balance of the heat passing from the flame to the fuel. Assuming that no exothermic or endothermic reactions take place in the solid propellant during heating, the heat balance is represented as follows:

$$h(T_f - T_s) = r_e \rho [c_{sp}(T_s - T_1)] \quad (1.40)$$

where:  $T_f$  = the flame temperature,

$T_s$  = the surface temperature of the burning fuel,

$\rho_c$  = the density of the fuel,

$c_{sp}$  = the specific heat of the solid fuel,

$T_1$  = the initial temperature of the fuel.

The expression in brackets represents the amount of heat absorbed by the fuel without the appearance of erosion.

From the last equation, we obtain

$$r_e = \frac{h(T_F - T_s)}{\rho_c c_{sp}(T_s - T_1)} = \frac{h}{\rho_c c_{sp}} \frac{(T_F - T_s)}{(T_s - T_1)} \quad (1.41)$$

Assuming that  $r_e = Kh$  in equation (1.34), then

$$K = \frac{r_e}{h} = \frac{1}{\rho_c c_{sp}} \frac{(T_F - T_s)}{(T_s - T)} \quad (1.42)$$

By substituting this  $K$  value in equation (1.38), we obtain

$$\alpha = \frac{0.0288 c_p^{0.2} Pr^{-0.667}}{\rho_c c_{sp}} \frac{(T_F - T_s)}{(T_s - T_1)} \quad (1.43)$$

In the case of combustion without erosion, we determine  $T_s$  by using the equation

$$r = a p^n$$

where the dependence of  $a$  on the temperature is expressed by the equation

$$a = \frac{b}{T_s - T_1}$$

In order to eliminate the unknown  $b$ ,  $a$  is designated for 2 temperatures, e.g.,  $+70^\circ\text{C}$  and  $-40^\circ\text{C}$ . Then

$$\frac{a_{+70}}{a_{-40}} = \frac{(T_s - T_{-40})}{(T_s - T_{+70})}$$

where only  $T_s$  is unknown.

In this manner the principal unknown  $K$  in the equation (1.34) is expressed by the corresponding set of temperatures. The other values that enter into the equation for  $a$  are known if the composition of the combustion gases is known. (The composition of the combustion gases can be calculated theoretically, using the method given in section 1.4.1.)

In this manner the calculated values  $a$  are close to the values calculated by

the trial method. For example, when  $\underline{a}$ , calculated by the last method equals  $2.25 \cdot 10^{-4}$ ,  $\underline{a}$  calculated by the trial method equals  $2.12 \cdot 10^{-4}$ . If we compare the results of the above-mentioned experimental method with the data resulting from the theoretically determined dependence, we find that the influence of the stream velocity on the burning rate in both cases is consistent approximately. On the other hand, a quite different temperature influence is observed. If we observe an insignificant temperature influence on the burning rate in the results of the experimental method, a quite significant temperature influence on the rate of erosive combustion will result from the derived equation.

The erosion over the entire length of the 100-cm charge is calculated and the erosion on the same charge when extinguished is measured on the basis of equation (1.39) [17]. The change in the cross-sectional area of the channel over the entire length (915 mm) of the grain, determined by calculation and measured after the grain is extinguished, is given in Figure 1.11. The initial cross-sectional area

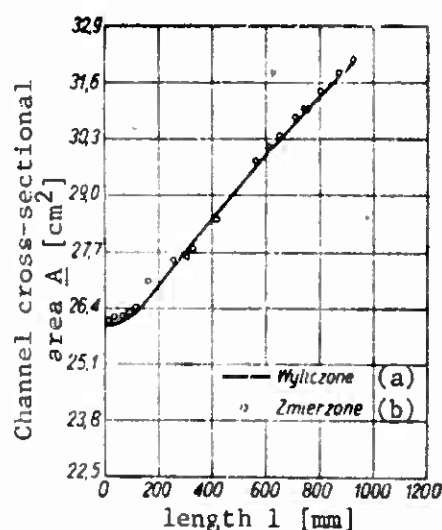


Figure 1.11. The results of interrupted combustion. The cross sectional area of the channel is a function of the charge length. Key: (a) = calculated and (b) = measured.

of the channel is  $13.6 \text{ cm}^2$  with a critical nozzle section area of  $13.9 \text{ cm}^2$ ; the burning time is 0.45 seconds and the diameter of the charge is 127.5 mm; the burning

rate at the beginning of the charge is 1.44 cm/second.

#### 1.6. Resonance Combustion

During the burning of solid propellants it happens that an unforeseen pressure jump occurs in the combustion chamber under certain conditions. This phenomenon is so unexpected that it occurs under combustion conditions that assure an equilibrium pressure in the chamber, under which another charge of the same fuel would burn well. This effect is called resonance combustion and is the result of an abnormal increase in the burning rate of the fuel. The resonance combustion effect occurs most frequently in the case of cylindrical charges. The pressure peaks which appear during resonance combustion can lead to a splitting of the grain, which in turn leads to destruction of the engine.

In experimentation, characteristic waves (an alternately rough and smooth surface) resembling standing waves are observed on the surface of the charge (particularly inside the channel) which had been burned under resonance combustion conditions, after it was extinguished. Thus, this suggests the assumption that the unstable combustion is caused by some resonance effect. This gave rise to the name of the phenomenon and established the orientation of studies on this effect, aimed at the detection of all possible vibrations occurring in the column and which may conjugate in the gas chamber.

A number of studies on the causes of the resonance phenomenon led [22,23] to the discovery that resonance combustion is caused by the formation of high-frequency pressure oscillations (fluctuations). These oscillations, which are difficult to detect on the ordinary gauges used in measuring the pressure curve in the combustion chamber, cause an increase in the burning rate of up to 150% under pressures above 120 atm [23]. Consequently, the equilibrium pressure in the combustion chamber is disturbed and this can be recorded on any gauge.

R. P. Smith and D. F. Sprenger [22] used an apparatus capable of measuring pressure fluctuations with frequencies up to 25 kilohertz in the chamber in their



experimentation. On the basis of their studies, they came to the conclusion that perturbations in the equilibrium pressure are always caused by oscillations having a high frequency and amplitude. These studies comprised a whole series of combustion tests on cylindrical charges inhibited on the outside and on the frontal surface so that combustion took place only on the internal surface. The charge was 50 cm long, the external diameter was about 6 cm and the internal (initial) diameter, 4 cm. During the burning of this charge, its internal diameter increased. By measuring the oscillations in the gas column, it was learned that the frequency of the oscillations decrease with increasing diameter of the internal channel of the charge (Figure 1.12).

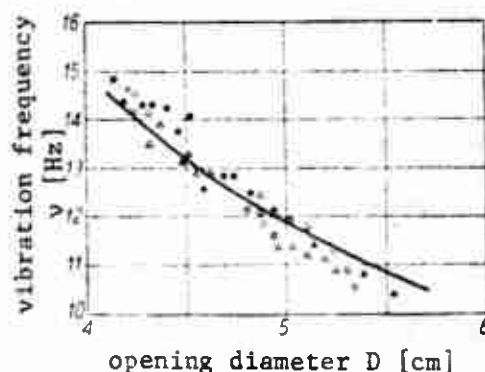


Figure 1.12. The dependency of the oscillation frequency on the opening diameter during unstable combustion. The experimental points were determined by various authors [13]. Key: the continuous line = theoretical data calculated with the equation

$$v_{10} = \alpha_{10} \frac{a}{D}$$

At the same time, calculations of the frequency of the specific oscillations of the gas filling these tubes were performed for the same type of tube, which formed the successively burned charges. The variation in the oscillation frequency with the change in opening diameter was in agreement with the theoretical calculations of the frequencies of the oscillations specific for the gases in the cylindrical space.

The same type of oscillations are present in a pipe organ. They are longitudinal waves, which may have a tangential, radial and axial nature. The specific oscillations in the tube are combinations of all these types of oscillations; however, it was determined that tangential oscillations predominate.

The frequency of the oscillations of each type can be determined [22] from the equation

$$\nu_{m,n,q} = \frac{a}{2L} \sqrt{\left(\frac{\alpha_{mn}}{R}\right)^2 + \left(\frac{q}{L}\right)^2} \quad (1.44)$$

where:  $m, n, q$  = the wave numbers (all positive or zero) corresponding to the tangential, radial and axial waves;

$a$  = the speed of sound in the considered medium;

$\alpha_{m,n}$  = the constant dependent on the  $m$  and  $n$  values;

$R$  and  $L$  = the radius and length, respectively, of the considered oscillating space.

In some cases it was learned that only one oscillation, corresponding to  $m = 1$  and  $n = 0$  ( $q = 0$ ), was present. In another case, oscillations corresponding to the first 5 values of  $m$  were detected. It is evident from this that in studies on the formation of resonance waves along the burning charge, particular attention should be devoted to the tangential-type wave. The frequency of this type of oscillation

TABLE 1.5. THE VALUES OF THE CONSTANT  $\alpha_{mn}$   
AS A FUNCTION OF THE WAVE NUMBERS  $m, n$

Values $\alpha_{mn}$				
$n \backslash m$	0	1	2	3
0	0.000	1.220	2.233	3.238
1	0.586	1.697	2.714	3.726
2	0.972	2.135	3.173	4.192
3	1.337	2.551	3.611	4.643

is not a function of the length, but only of the wave number  $m$ , the radius of the tube and the speed of sound in the medium, which can be expressed by the equation

$$\nu_m = \frac{a_{tm}}{2R}$$

These same authors studied the oscillations in the ring section space. The frequency of the tangential oscillations for this space is determined from the equation

$$\nu_{m,0,0} = \frac{\alpha_{m0}}{(R_i + R_o)}$$

where  $R_i$  and  $R_o$  are the internal and external diameters of the ring.

The latter equation is valid when  $R_o/R_i > 4$ , which is verified also by experimentation. Because the sum,  $R_o + R_i$ , does not vary during combustion in the ring section space, the frequency of the tangential oscillations is also a constant.

Some of the conclusions of Smith and Sprenger are confirmed in more recent publications [23], where it is also stated that no transverse, but only longitudinal waves were detected in the engine. It was also learned that sound vibrations have no decisive effect on the combustion stability. In this manner Smith and Sprenger [22] quite comprehensively studied and mathematically treated the high-frequency oscillations occurring during combustion as a cause of the so-called resonance combustion. Nevertheless, 2 principal problems of this phenomenon have not yet been explained [29]: (1) the causes of the high-frequency oscillations have not been explained thoroughly and with complete certainty; (2) the mechanism of such a substantial increase in the burning rate, which is considerably greater in the case of resonance vibrations than that calculated with combustion laws for the average pressure, has not been adequately explained.

At the present time there are many publications dealing with study methods leading to the detection of the causes of resonance combustion. However, there is still no generalized opinion nor is there even a precise quantitative approach to

this problem. The reason for this lies in the fact that there are a great many parameters, upon which the high-frequency vibrations causing the resonance combustion can depend, e.g., the composition of the fuel, its structure (colloidal or composite), the geometry of the charge and chamber, the combustion pressure, the burning rate, the heat value of the fuel, etc. It has been learned that, in general, fuels with a high energy index, such as ballistes, propellants containing  $\text{NH}_4\text{ClO}_4$ , etc., are much more prone to unstable combustion than fuels with a lesser energy content. Nevertheless, as experimentation has indicated, this factor alone is not sufficient.

Some authors are of the opinion that the tendency of the fuel to burn unevenly increases with increasing burning rate. However, it has been shown that the burning rate cannot be an unequivocal index of the tendency of the propellant to resonance combustion either; for example, fast-burning  $\text{KClO}_4$ -based propellants are less prone to unstable combustion than slow-burning  $\text{NH}_4\text{ClO}_4$ -based fuels. Moreover, the burning rate increases with increasing energy indices; therefore, it is sometimes difficult to determine which is the cause of combustion instability: the energy indices or the burning rate.

In the case of composite propellants, the unstable combustion can be a function of the granulation and crystal structure of the oxidizer crystals. However, the burning rate varies with varying granulation of the oxidizing substance. Therefore, it is difficult in this case also to determine whether the granulation or the burning rate is directly decisive in the tendency of the fuel to resonant combustion.

In one of numerous studies an attempt was made to determine whether and how the concentration and size of the oxidizer crystals in composite-type propellants influence the generation of resonant combustion [23]. Propellants, in which  $\text{NH}_4\text{ClO}_4$  crystals constituted the oxidizing substance, were subjected to testing. The first series of tests were designed to study the effect of the percent of oxidizer content on combustion instability. The perchlorate granulations were close to the technological limits of possibility. Four propellants were studied (Table 1.6). The

TABLE 1.6. THE PROPERTIES OF PROPELLANTS STUDIED FOR RESONANT COMBUSTION

	Propellant			
	A	B	C	D
Total amount of oxidizer, %	70	75	80	85
Density, g/cm <sup>3</sup>	1.605	1.647	1.704	1.760
Mean molecular weight of the combustion products	21.9	23.6	25.5	27.2
Heat of explosion, cal/g	698	864	1,010	1,050
Specific impulse, kg·sec/kg	211	226	239	251

granulation ranged from a few to 300 microns. Propellant A had the finest crystals and propellant D the coarsest. Because of the difference in granulation, the burning rate of all the fuels was approximately identical. Combustion tests showed that propellant A does not exhibit the property of irregular combustion; on the other hand, the fuels with greater energy values (B and C) exhibit irregular combustion toward the end of burning. In propellants B and C, secondary pressure jumps are observed on the pressure curve over time. In contrast to the primary jumps (ignition jump), they are caused, as the authors have concluded, by a nonuniform blending of the mass during production of the propellant.

The possibility of a nonuniformity of this type is less in fuels with a greater  $\text{NH}_4\text{ClO}_4$  content, because here there is a maximum amount of oxidizer in the entire mass. The authors explain the greatest regularity of combustion of propellant D on the basis of this, among other factors, in spite of its being the most energetic fuel. The lower burning rate of propellant D in comparison with propellant C could be another factor affecting the regularity of combustion. Accordingly, the rate of energy release in propellant D was comparatively low. This latter factor (rate of energy release) is considered by the authors to be the most important because it comprises the energy content, burning rate of the propellant and the composition.

Another series of tests embraced the study of propellants with identical energy contents (all with 76%  $\text{NH}_4\text{ClO}_4$ ) but with distinctly different granulations (Figure 1.13). This test series demonstrated that the propellant with the finest granule size (J) exhibited the highest burning rate and the greatest tendency to irregular

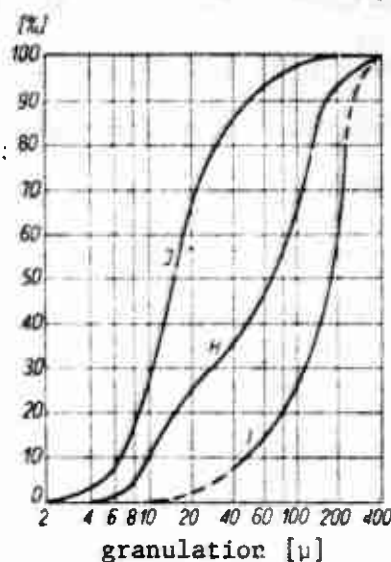


Figure 1.13. Granulation (comminution) of the oxidizing substance of propellants studied for resonant combustion.

combustion. Propellant H burned considerably more regularly. When the propellant with the largest crystals (I) was burned, it was noted that there was an excessively high pressure in the initial combustion phase in some charges; this can be explained by the nonhomogeneity of the propellant, which is difficult to achieve, particularly with the large crystals. Accordingly, the conclusion drawn from the first test series is confirmed in the second series, where propellant J has the highest rate of energy release and therefore has a tendency to unstable combustion; thus, the influence of the heat value, burning rate and structure of the propellant on unstable combustion can be replaced by one indicator: the influence of the rate of energy release. Therefore, it is useful to specify the rate of energy release (in kcal) from a unit of surface area per unit time when giving the properties and parameters of the given propellant. This individual value could be considered as a certain index



of the propensity of the propellant to resonant combustion. Obviously, this value should be related to the pressure and other conditions corresponding to stable combustion.

As already stated, the geometry of the charge and the combustion chamber also has an effect on the combustion instability. It was found [19] that the resonant combustion phenomenon occurs most frequently, although not exclusively, in cylindrical charges. Resonant combustion depends on the location of the critical point, among other factors, at which the gas velocity is equal to zero. This is explained by the fact that if some perturbations in the pressure arise at some point where the gas velocity is high, the vibrations will be carried outside of the charge even before high amplitudes appear. The time required for the formation of such amplitudes is sufficiently long at the point of zero velocity and near it. The critical point always develops in the case of cylindrical grains. The gas fraction developing on the combustion surface travels in the direction of the nozzle via the space between the chamber walls and the external walls of the charge while the other fraction proceeds through the central channel of the charge. The point of zero velocity is located at the site of origin of these two gas streams. As a function of the dimensions of the charge and chamber, this critical point can be placed inside the charge opening, at the bottom of the chamber (behind the charge) or in the space between the walls of the chamber and charge. This depends on the relationship of the combustion surface to the cross-sectional area of the channel and the space between the chamber wall and the external wall of the charge.

If the inequality is maintained

$$\frac{\pi D_k L}{\frac{\pi}{4} (D_k^2 - D_z^2)} > \frac{\pi d L}{\frac{\pi}{4} d^2}$$

where:  $L$  = the length of the charge;

$D_k, D_z$  = the diameter of the chamber and the external diameter of the charge, respectively;

$d$  = the internal diameter of the charge,  
 then the fraction of gases evolving on the external walls of the grain must pass through the central channel in order to achieve the conditions of an identical ratio of burning surface to discharge surface everywhere. The zero gas velocity point for these conditions is located in the space between the walls of the chamber and the charge (Figure 1.14).

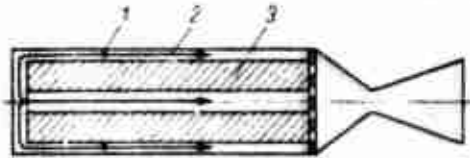


Figure 1.14. The effect of development of the zero gas velocity point. Key: 1 = zero velocity point on the periphery of the charge; 2 = the gas stream; and 3 = the charge.

In the other case, if the inequality

$$\frac{\pi D_s L}{4 (D_s^2 - D_i^2)} < \frac{\pi d l}{4}$$

is maintained, the fraction of gases from the central channel will travel out through the space between the walls of the chamber and charge. In this case the zero gas velocity point lies inside the charge. As demonstrated by experimentation, such a situation is highly disadvantageous. Sometimes, it may even occur [24] that this is the only case in which resonance vibrations develop in the cylindrical charge. Gases at the critical point, located in the charge opening, readily lapse into resonance vibrations, which in turn give rise to a more rapid combustion and thereby a pressure increase which may lead to destruction of the engine. Sometimes these vibrations cause a disintegration of the charge grain and an explosion (when the mechanical strength of the grain is insufficient). The zero velocity points can also cause resonant vibrations, even in the first case; however, experimentation

[19] has shown that explosions then occur more rarely.

The third possibility is the location of the critical point at the bottom of the combustion chamber. This occurs when

$$\frac{\pi D_1 L}{4(D_1^2 - D_2^2)} = \frac{\pi d L}{4d^2}$$

It was learned by experimentation that it is possible to prevent resonant combustion by boring radial holes in the grain, by placing a noninflammable rod in the channel and by employing a channel with a nonround cross section. All these data are used in rocket technology but they do not explain the real reason for vibration development in the combustion center. Of course, it does explain [25] the generation of more powerful vibrations from small perturbations, but it is difficult to explain the origin of these small disturbances, probably because the causes are manifold. H. Graß suggests that a slight pressure increase leads to a localized increase in the burning rate, which in turn increases the pressure, which again causes an increase in the burning rate, and so forth. In this manner, if only pressure vibrations arise, their amplitude increases continuously with time. Another question which we have already mentioned and which has not yet been fully explained is the increase in the burning rate (not proportional to the pressure) during resonance combustion. It is generally possible to explain this by the fact that heat conduction from the flame to the propellant increases with the appearance of the vibrations, and then the burning rate increases not only because of the increase in the mean pressure but also because of the rise in temperature of the charge surface.

#### 1.7. Discontinuous Combustion ("Sneeze")

In the propellant combustion process it is observed that if the pressure in the rocket motor falls below a certain critical value, it immediately drops to atmospheric pressure and combustion ceases. After a fraction of a second or after several seconds, combustion resumes and the entire process is repeated. This phenomenon

resembles sneezing, thus its name.

"Sneezing" occurs particularly when the critical nozzle cross section (throat) is too large in relation to the burning surface of the charge, and specifically when this throat size produces a pressure which barely reaches the above-mentioned critical pressure. In this case, even slight perturbations cause sudden pressure drops to the atmospheric value, heat does not flow from the combustion zone to the charge and the charge becomes extinguished. However, the temperature of the external layers will still be sufficiently high for a certain period of time. In addition, certain exothermic reactions occurring in the subsurface zone and heat transmitted from the engine walls cause renewed ignition of the propellant. The combustion on the heated layer of the propellant proceeds sufficiently intensely; however, when only this external layer is burning, the burning rate decreases, the pressure in the engine drops and the cycle repeats itself. Although the principal cause of this effect lies in the pressure drop below the critical point, renewal of ignition depends on whether the transformations taking place under the influence of temperature in the subsurface zone are exothermic. Thus, the phenomenon essentially depends also on the chemical composition of the propellant.

#### 1.8. Geometry of the Charge

Solid propellant rocket engines have their principal characteristics, such as the work time, magnitude of thrust, combustion chamber pressure and others, determined by the respective configuration of the charge. It is well known that the said characteristics are dictated in liquid-fuel engines by auxiliary mechanical devices which regulate the fuel supply to the combustion chamber. The absence of these auxiliary devices in solid-propellant engines is one of their advantages with respect to liquid-fuel engines. However, it should be remembered that the same problem of determining the characteristics of the engine remained but it was transferred from the engine construction itself to the propellant.

The respective performance characteristics of the engine are taken into account

in designing the configuration of the propellant. Therefore, the design of the fuel charge for solid propellant engines is a problem of extreme importance. In each charge configuration design, the propellant mass must fulfil the conditions defined in the so-called combustion law of fuels (powders). This law states that the propellant must burn over the entire available surface in layers parallel to the primary configuration, i.e., the burning rate is identical over the entire surface. The fulfillment of this condition must be achieved in the technological process of the propellant by making it homogeneous and avoiding air pockets. The technological processes employed to achieve this are described in subsequent chapters.

The existing charge configurations can in general be divided into 3 types with respect to surface changes during combustion: (1) combustion with a practically constant combustion surface, (2) combustion with a decreasing combustion surface area (degressive), and (3) combustion with an increasing combustion surface area (progressive).

Change of the combustion surface in time is evident in the pressure and time curves in Figure 1.15.

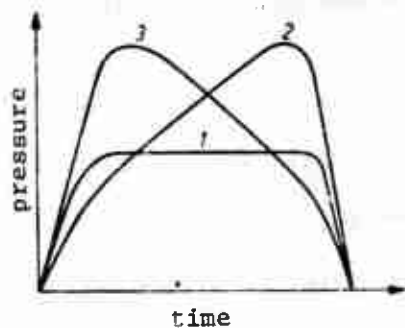


Figure 1.15. The basic combustion types.  
Key: 1 = combustion with a constant burning surface area; 2 = progressive combustion; 3 = degressive combustion.

The curve for the charge with a constant combustion surface area indicates that the pressure is constant for practically the entire period of time. This is very desirable because the engine functions reliably only if the maximum pressure is less

than the maximum permitted and greater than the minimum allowed (in the case of the minimum pressure). Thus, in practice it is still highly desirable to achieve a constant combustion surface area during the entire work time of the engine.

The desired combustion surface area and its time change curve can be achieved by: (1) selection of the appropriate surface shape of the propellant charge and (2) covering some surfaces of the charge with a special noncombustible layer which inhibits burning of the charge on these surfaces, in other words, a so-called armor plating or shielding of the charge.

The noncombustible material used for the shielding is called an inhibitor. The most typical charge configurations and their respective pressure-over-time curves are given in Table 1.7 (12 examples). A great many geometrical configuration combinations are possible. Each propellant charge configuration has its advantages and disadvantages which are correspondingly exploited to best advantage in engines for various purposes. The charge in the form of a solid cylinder is seldom used because of its distinctly degressive combustion, and this only in connection with a distinctly progressive charge (example 7). Charges that are only end-burning (example 2) are used in engines with a small thrust and a long work time. Engines with such charges are used as sustainer motors in two-stage rockets. In order to achieve greater thrusts, these motors have a large chamber diameter and a quite substantial passive weight (due to the strong heating effect the chamber walls are thick). In addition, this engine has the disadvantage that its center of gravity shifts during operation, which is obviously reflected in flight stability. However, this type of charge is frequently used, particularly in the case of fast-burning propellants which furnish a rather large thrust because of their charging density<sup>8</sup>. All engines with charges burning on their lateral surfaces have a lower charging density and a shorter work time, but they can furnish large thrusts. Various lateral-burning charge combinations make it possible to achieve the most divergent pressure-over-

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<sup>8</sup> See page 86.



TABLE 1.7. A COMPARISON OF THE SURFACE SHAPES OF SOLID ROCKET PROPELLANT CHARGES














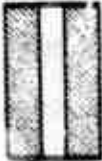


















Propellant number	Description of charge or name of configuration	Cross section	Longitudinal section	Pressure curve in time	Remarks
1	Charge in the form of a solid cylinder				
2	Charge in the form of a solid cylinder, shielded on the lateral surface				1 = inhibitor; 2 = propellant
3	Tubular charge, shielded on the lateral surfaces				
4	Unshielded tubular charge				
5	Tubular charge shielded on the external surfaces				
6	Charge with cross-shaped cross section, shielded on the projections				

TABLE 1.7. (continued)

Propellant number	Description of charge or name of configuration	Cross section	Longitudinal section	Pressure curve in time	Remarks
7	Charge with a ring cross section, inhibited outside of the cylinder in the center				
8	Charge with a cylindrical-conical channel				1 = thrust from the cylindrical portion, 2 = thrust from the conical portion
9	A cigar-shaped charge with a cylindrical channel, shielded on the outside				
10	Charge with a star-shaped channel, inhibited on the outside				
11	A multi-channel charge, shielded on the external surface				
12	Charge with a wagon wheel cross section				

time characteristic curves. These charges can be of 2 types: (1) those which do not protect the chamber walls against heat (examples 1, 2, 3, 4, 6, 8 and 9); and (2) those which protect the chamber walls against the direct action of the flame (examples 5, 7, 10, 11 and 12).

This fact is an important consideration because the strength of the walls decreases abruptly with their increasing temperature. This situation occurs when there is no insulating layer between the combustion surface and the engine walls. In such engines the chamber walls must be correspondingly thickened in order to have sufficient strength at high temperatures. This causes an increase in the passive weight of the rocket, which constitutes an important disadvantage in this type of charge. In the case of charges 5, 7, 10, 11 and 12, the chamber walls do not become heated because the flame has no access to them until the end of combustion. The layer insulating the chamber walls from the flame here is a layer of propellant and a layer of inhibitor (shielding factor). The combustion chamber walls can be thin, calculated with the strength of the cold material. Thus, if we have additional stipulations to follow with respect to shielding and protection of the chamber walls against heat in designing the surface shape of the charge, the number of forms which may be chosen is reduced.

Modern rocket engines employ charges with configurations which protect the walls against heating and assure thrust constancy (examples 7, 10, 11 and 12). Configurations with cross-shaped and cigar-shaped cross sections and charges with a cylindrical-conical channel do not protect the chamber walls against heating, in spite of the fact that they have a shielding layer on the external lateral surface.

The combustion surface variation and thrust curves in time frequently are quite complex, e.g., for the cigar-shaped configuration or that with a cylindrical-conical channel, they depend on the angle of inclination of the cone, which must be different for different length of overall charge in order to maintain combustion surface constancy.

In the case of the configuration with a cross-shaped cross section shielded on

the projections, the combustion is progressive; in the unshielded case, the combustion is distinctly degressive. In connection with this, partial inhibitions of the projections make it possible to regulate the combustion curve at will.

Charges which burn internally and which have no projections on the circumference of the internal channel always have a progressive-type combustion; on the other hand, for charges which burn only on the external surface and have no projections, the combustion is of the degressive type. Thus, when the problem of isolating the chamber walls from the combustion zone with a layer of charge was posed, it was necessary to design a charge which burned exclusively from the internal side of the channel with a constant combustion surface. In order to maintain combustion surface constancy, it is necessary to provide internal projections in the channel. This is why we have charge designs with star-shaped channels, with channels in the form of a wagon wheel (example 12) and those with a number of channels.

Mathematical calculations on the shape and number of the projections in the star-shaped charge channel constitute a rather complex problem, primarily because the number of cross-sectional channel configurations which assure combustion surface constancy is practically infinite. Therefore, the problem is solved by the trial and error method with the prior assumption of several parameters. A mathematical description of even the most common channel cross-sectional configurations would exceed the bounds of this work. Data on some typical configurations are frequently given in tables or graphs [7].

In the case of configurations that do not assure protection of the chamber walls against heating, it is a simple matter to determine the geometrical dimensions which assure the combustion surface constant.

The most frequently used surface shape of this charge group is the cylindrical one. The surface area of such a charge after shielding the frontal surface is

$$S = \pi L (D_0 + D_1)$$

where:  $L$  = the length of the charge;

$D_0$  = external charge diameter;

$D_1$  = internal charge diameter.

Another frequently used surface shape of the charge group which protect the chamber walls against heat is the star-shaped form. Thus, cylindrical charges or charges with a channel having a star-shaped cross section are most frequently referred to in deliberations on charge technology and on the combustion process.

The length to diameter ratio can be different for both of these cases. However, it appears that for an assumed length there is a certain optimal diameter value at which the energy contained in the fuel will be most advantageously exploited. Likewise, there is a certain optimal length for an assumed diameter. When the length is greater than the optimal, the percent share of the chamber weight in relation to the fuel increases. Then we say that the engine has a large passive weight. If the charge is shorter than the optimal, the excessively large engine diameter in relation to the propellant weight causes a large air resistance to be posed on the rocket during flight, whereby the fuel supply is not exploited to the greatest advantage in increasing the range of the rocket. This optimal length can be calculated only after making allowance for the resistances encountered by the engine during flight, chamber wall strength, specific weight of the chamber walls, the pressure prevailing in the chamber, etc. Thus, the problem of selecting the optimal length and diameter measurements of the rocket lies in the field of internal and external ballistics [7].

The magnitude of the external and internal diameters of the cylindrical charge must also be appropriately related to the diameter of the combustion chamber; this will be discussed in subsequent sections.

In the case of a charge with a star-shaped channel, it is assumed as a condition of channel size that the thickness of the combustion layer  $e$  cannot be greater than half the chamber radius  $R_k$ . Only in exceptional cases is  $e$  equal to  $0.7 R_k$ .

Sometimes a charge that furnishes 2 types of thrusts can be used. A charge of this type is comprised of 2 layers of different propellants. First, the one layer

is burned, furnishing a certain definite thrust (e.g., starting thrust) and then the second layer, which supplies an entirely different thrust (sustaining). Such a combination of 2 or even several different propellants theoretically can be used in all the above-cited surface shapes.

#### Footnotes

1. to p. 34. The reader will find precise data on nozzle design in numerous publications [7,30].
2. to p. 45. Sprawoznik Khimika. Gosudarstvenoye Khimicheskoye Izdatel'stvo, Moscow-Leningrad, 1952.
3. to p. 46. Detailed data can be found in the book by W. Kozakiewicz [30].
4. to p. 49. Kalendarz Chemiczny, Vol. I, p. 422. PWT. Warsaw, 1954.
5. to p. 51. Measured in the original.
6. to p. 63.  $Re = \frac{DU\rho}{\mu} = \frac{DU\gamma}{\mu g} = \frac{DG}{\mu g} = \frac{DU}{\lambda}$

where: D = the stream diameter; U = linear velocity;  $\rho$  = density;  $\mu$  = absolute viscosity;  $\gamma$  = specific gravity; and  $\lambda$  = kinematic viscosity.

7. to p. 63.  $Pr = c\mu g/\lambda$ , where c = the specific heat; and  $\lambda$  = specific thermal conductivity.
8. to p. 79. The charging density is the ratio of the charge mass to the chamber volume of the engine.



## 2. PROPELLANT FOR THE ROCKET ENGINE

Designing the surface shape of the propellant charge is intimately associated with the designing of the entire engine. Therefore, anyone working on problems connected with the propellant must be at least qualitatively familiar with this designing.

In this section particular consideration will be given to the parameters directly connected with the propellant, and the indispensable formulae of internal ballistics are cited without derivation but only with a complete description. Precise information on the internal ballistics of solid propellant rocket engines can be found in numerous foreign as well as domestic publications [30]. The externally and internally burning cylindrical charge is considered below as a classic example; it is the one most frequently used in the study of new propellants.

The constants,  $K_I$ ,  $K_n$  and  $J$ , are used in determining the combustion conditions. These constants are expressed by the following formulae:

$$K_I = \frac{A_{sp}}{A_p}; \quad K_n = \frac{A_{sp}}{A_{cr}}; \quad J = \frac{K_I}{K_n} = \frac{A_{cr}}{A_p}$$

where:  $A_{sp}$  = the combustion surface of the charge;

$A_p = A_o - A_{po}$  = the cross-sectional area through the channel of free flow,

in which:

$A_o$  = the cross-sectional area of the chamber;

$A_{po}$  = the cross-sectional area of the grain;

$A_{cr}$  = the critical cross-sectional area of the nozzle;

$K_I$  = internal contraction\* constant;

$K_n$  = contraction constant.

All the  $K_I$ ,  $K_n$ ,  $K_I/K_n$  relationships are determined for an optimal pressure in

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\*Translator's note: We cannot confirm this.

the combustion chamber.

The pressure at which combustion is stable and which assures a maximum total impulse with minimum engine weight is called the optimal pressure [7].  $K_I$  is determined as a function of the grain type, the gas pressure in the combustion chamber, the form of the charge and other factors. The larger the  $K_I$  value, the greater the velocity of the gas stream along the charge and the more difficult it is to assure regular (stable) combustion. The constants  $K_I$  and  $K_n$  are determined experimentally for the individual propellants and they are a linear function of the burning rate  $\underline{r}$ .

The burning rate  $\underline{r}$  is determined in the so-called Crawford bomb (Figure 2.1), in which a bar of the propellant is burned on the frontal surface (the lateral surfaces are inhibited) under constant pressure. Two wires which form 2 corresponding circuits in the timer are spaced in the bar a certain precisely-defined distance apart. The wires are designed so they burn off when the propellant bar is burned. When the first wire is burned off, the timer is set in motion and when the second is burned off, the timer stops. The burning rate  $\underline{r}$  is calculated by the distance between the wires and the recorded burning time.

Burning in the Crawford bomb is carried out in an atmosphere of inert gas (nitrogen). The pressure is regulated by an automatic pressure regulator or by the use of a large vacuum chamber. Thus, if the burning rate of the given propellant is known, we can forecast the  $K_n$  value approximately (on the basis of comparisons with known propellants); however, an accurate determination is usually made by combustion in a chamber with a nozzle. (The burning rate measured in a Crawford bomb sometimes differs from that obtained in a chamber with a nozzle.)

The combustion surface area of the charge is calculated from the assumed surface shape. In solid propellant rocket engines  $K_n$  values of 200-2,000 are used, depending on the type of propellant. It was experimentally determined that

$$K_I \leq 0.5 K_n \quad \text{and} \quad A_{cr} \leq 0.5 A_p$$

Thus,  $K_n$  and  $J$  are still the principal indicators for good choice of the charge

for the chamber. The equilibrium pressure in the combustion chamber depends to a great extent on these values. Therefore, if these values are not properly chosen, the equilibrium pressure will not be constant. As  $A_p$  increases in relation to the invariable  $A_{cr}$  or if  $J$  decreases and, in connection with this, the erosion is less, the burning is slower and the pressure has a lower value than that which is obtained in calculations which take the erosion into account. The cross-sectional area of the channel is variable during combustion and this causes a variance in the flow rate of the combustion gases and a pressure drop, not only of the mean pressure but also in the pressure differences along the axis of the engine.

In the final combustion phase where  $A_p = A_o$ , the  $J$  ratio assumes its minimum value and the pressure difference in the front portion of the chamber and at the nozzle is at its least value.

In the initial combustion phase, when the thickness of the burned layer is equal to zero, i.e., at the moment of ignition, the pressure difference between the front and back portions of the chamber is the greatest. This pressure difference and the frictional force of the gases flowing out along the lateral surfaces of the charge can cause the charge to press against the back grate in the case of the cylindrical charge. Because the pressure difference is greatest at the beginning of combustion and because the pressure increases rather violently, a dynamic force acts on the charge in a longitudinal direction at the moment of ignition. This "impact" in the case of a brittle mass can cause a cracking of the charge, particularly if it is not in contact with the grate before ignition (the charge then acquires acceleration and strikes against the grate), or a swelling of the charge in the case of an elastic mass. Cracking of the charge leads to an abrupt increase in the combustion surface area and, thereby, also in the pressure which usually ends in tearing out the safety devices (from the research viewpoint) or disintegration of the chamber. A swelling of the charge causes a decrease in  $A_p$ , which signifies an increase in  $K_I$  and  $J$ . Thus, it is necessary to take into account the possible charge deformations during combustion in determining the constants  $K_I$ ,  $K_n$  and  $J$ .

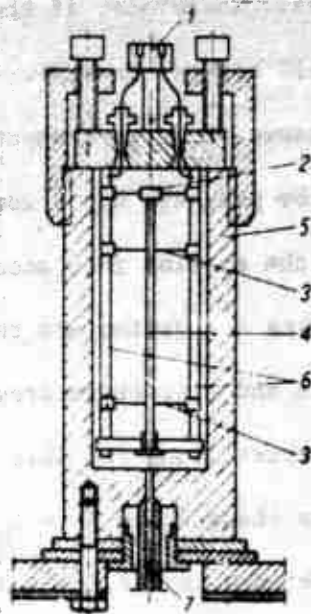


Figure 2.1. Crawford bomb. Key: 1 = electric contact; 2 = ignition wire; 3 = timer wires; 4 = propellant bar; 5 = chamber; 6 = bar supporting brackets; 7 = nitrogen or reducer feed.

Some authors use the value  $1/J$  [7]. This value must be always greater than unity; most frequently, it falls within the limits 1.5-2.5. The  $1/J$  value may reach 5 and even higher for engines with low work parameters. In order to increase the charge density, this ratio should be as small as possible, but with respect to combustion stability, this minimal value must be determined experimentally. A small  $1/J$  value gives rise to a pressure peak at the beginning of combustion.

It should be mentioned that when working on new fuels for solid propellant rockets, it is necessary to take into account the energy content of the propellant, its mechanical strength, the dependence of the burning rate on the pressure (exponent  $n$ ) and the temperature and such factors as the technology and availability of the raw materials.

The following sequence is usually maintained in the development of new propellant compositions:

1. Preparation of the appropriate mixture having the specified stoichiometric

composition.

2. Determination of the energy content of the given propellant composition (analytically or experimentally).
3. Determination of the burning rate and the power exponent in the Crawford bomb.
4. Orientational determination of  $K_n$  by analogy with known propellants whose  $K_n$  values are known, at a known burning rate.
5. Orientational determination of  $K_I$  from the inequality  $K_I \leq 0.5 K_n$ .
6. Orientational determination of the ratio  $J = K_I/K_n = A_{cr}/A_p$ .
7. Preparation of an appropriate charge for a known engine on an experimental basis with a nozzle having a critical cross section  $A_{cr}$ .

In the study of a propellant it is often necessary to consider the internal ballistics accurately [30] as well as the technological data on an engine.

#### 2.1. Construction of the Engine

The most important elements of engine construction are the nozzle and the combustion chamber.

In solid propellant engines the nozzles are not cooled as in liquid fuel engines (the lack of a cooling medium, which in liquid fuel engines is constituted by the liquid components of the fuel). In connection with this, it is necessary to protect the nozzle against burning out by other means. One of these is the employment of high-melting materials, such as graphite, molybdenum and others in constructing the critical nozzle cross section. Another method is the use of average-melting materials with a high specific heat for nozzle construction; then when the nozzle has a correspondingly high weight, the heat is readily conducted away from the critical cross section and is not liable to burn out. The disadvantage inherent in this latter method is excessively large nozzle weight, as the nozzle must have a large heat capacity, and this increases the passive weight of the engine. The first method is not too good either, particularly with longer engine work times (40-60

seconds) and with high-energy fuels. Therefore, the problem of nozzle protection in solid propellant engines is still a pressing one. Some authors [7] propose membrane (shell) cooling or cooling by utilizing the heat of evaporation of the substance.

Another engine construction element is the chamber, the parameters of which are also dictated by the requirements of the propellant. The combustion chamber is a thin-walled cylinder. The thickness of the walls  $h$  is determined by means of the equation

$$h = \frac{p_c R_c}{\sigma} \quad (2.1)$$

where:  $p_c$  = the pressure in the chamber;

$R_c$  = the radius of the chamber;

$\sigma$  = permissible stress on chamber material.

Such a chamber-wall thickness obviously does not take into account a weakening of the chamber due to attachments nor does it take into consideration the bending moments which occur during rocket flight or the heat stresses which may occur during operation of the engine. Thus, the chamber-wall thicknesses calculated with the said equation must be chosen with appropriate reserve. In addition, it is frequently necessary to make the walls thicker for the simple reason that the thicknesses arising from the calculations are so small that they are technologically impossible to produce. The following example illustrates this quite well:

$$\sigma = 10,000 \text{ kg/cm}^2$$

$$R_c = 20 \text{ cm}$$

$$p_c = 50 \text{ kg/cm}^2$$

$$h = \frac{p_c R_c}{\sigma} = \frac{1,000}{10,000} = 0.1 \text{ cm}$$

A wall that is this thin may have a definite, comparatively quite large deflection. Therefore, the wall is made that much thicker so that the technological



deflections lie above this thickness of 0.1 cm.

In considering the problem of reducing the passive weight of the chamber, it should be stressed that it is proportional to the wall thickness  $h$  and the specific gravity of the chamber material  $\gamma$ .

The wall thickness is inversely proportional to the allowable stress  $\sigma$ ; therefore, a passive weight reduction occurs when the ratio  $\sigma/\gamma$  has a maximum value. A comparison of several chamber construction materials with their permissible stresses, densities and the so-called specific strength of  $\sigma/\gamma$  are presented in Table 2.1.

TABLE 2.1. THE MECHANICAL PROPERTIES OF SOME STRUCTURAL MATERIALS

Material	Permissible stress (kg/cm <sup>2</sup> )	Specific gravity (kg/cm <sup>3</sup> )	Specific strength $\sigma/\gamma$ (cm)
Normalized steel 4130	6,500	0.00784	829,000
Heat-treated steel 4130	12,500	0.00784	1,590,000
High grade steel	19,000	0.00784	2,425,000
Aluminum alloy 75 ST	6,000	0.00277	2,166,000
Titanium alloy	6,500	0.00443	1,467,000
Phenol or epoxy plastic, reinforced with glass fiber (currently produced)	4,000	0.00166	2,410,000
Plastic reinforced with glass fiber (in the future)	6,000	0.00180	3,333,000

in accordance with [7]. It is apparent from the table that some materials are better than steels in some cases in spite of the fact that they have permissible stresses which are comparable to low steels. New titanium alloys may also have a very high specific strength.

In the table the parameters of the materials are cited for normal temperatures. When the temperature is raised, the strength of the material decreases, and this takes place much more extensively for synthetic substances than for metals. In



addition, the property variation in the particular production grades and in the finished products is greater for synthetic materials than for metals. Likewise, the stability (property variation in time) of the mechanical properties of plastics is much poorer than the stability of metallic alloys. Therefore, synthetic materials have not yet enjoyed wide usage as the choice for rocket engine chambers. If the utilization of these substances is proposed, it is only in cases where protection of the chamber against heating is desirable. This takes place in charges which burn from the center and which are affixed to the walls, where the fuel and the inhibiting layer serve to insulate the chamber walls from heat. Because there has been a distinct tendency to employ this type of charge, this has made it possible to also have an increasingly greater application of fiberglass-reinforced synthetic materials for combustion chamber construction.

At the present time heat treated steel is most frequently used in chamber construction. However, it is gradually being displaced by fiberglass-reinforced materials. In the perspective sense, consideration can be given to laminated materials consisting of alternate layers of plastics and steels. The cermets are frequently used in the construction of smaller-caliber rocket chambers.

In the production of thin-walled chambers from heat treated steels the most frequently used methods are either deep stamped or bended sheets, which then must be welded. Deep stamping is advantageous in that it is possible to shape the variable wall thickness in accordance with requirements (thicker in the front portion). When a chamber is shaped from sheets, the bottom must be either welded or fastened with screws. Fiberglass-reinforced plastic materials for chamber construction consist of glass fibers spun into threads and impregnated with the substance. In order to obtain a greater chamber strength, the glass fibers must be precisely oriented in accordance with the prevailing loads. The chamber can be constructed by winding the glass threads on an appropriate form and then impregnating the wound layer with a plastic [16]. Particular attention must be given to joining the metal bottom to the cylindrical portion of the chamber fabricated from this material.

## 2.2. Selection of Inhibitor

In research on propellants, we encounter the problem of selecting the type of inhibiting substance as well as the problem of causing the charge to adhere to the chamber walls. The inhibiting substance is usually a compound with characteristics similar to those of the given propellant. For example, for the inhibition of colloidal propellants, such as cordite I.P.N. and others, cellulose acetate is often used; in the case of asphalt-based propellants, bituminous compounds with petroleum are used [33]. In the case of composite fuels with a butadiene rubber base, a layer of rubber forms the inhibiting layer. The chemical similarity of the inhibitor and fuel assures a good mutual adhesion.

The inhibitor layer is applied either by coating the surface of the charge with a solution of the inhibitor, by causing a prepared layer to adhere to the charge, by coating it with a monomer which polymerizes on the surface or by coating it with the inhibitor in a molten state. The application of a coating by solution is inconvenient because the solvent must be evaporated off, and therefore only a very thin layer can be deposited at a time. In order to secure good inhibition, it is necessary to successively apply several layers. When the finished inhibitor layer is made to adhere, the quality of inhibition depends exclusively on the quality of adhesion. The most convenient method is the application of a liquid monomer coat which hardens on the surface of the charge.

From the mechanical point of view, the inhibitor layer should be sufficiently resistant and elastic, similar in mechanical properties to the fuel itself. In the case of elastic fuels, e.g., in the case of a front (end)-burning charge, the charge "swells" under the effect of the compression force; the inhibitor, therefore, may not crack but should be capable of expansion. In the case of charges which adhere to the chamber walls, the inhibitor should adhere well to metals and have good elasticity. Elasticity is necessary here because the mutually adherent metal and inhibitor layer with widely divergent coefficients of thermal expansion can give rise

to internal stresses when the temperature changes, which in turn would lead to the appearance of cracks in the casing of the grain. Just as the fuel, the inhibitor should alter its mechanical properties as little as possible with a change in temperature within the range  $-40$  to  $+50^{\circ}\text{C}$ . A good inhibition of the charge surface, which assures functioning of the engine for a period of 10-20 seconds, is difficult to obtain, especially if the stream of hot gases flows around the inhibitor layer.

### 2.3. Ignition of the Fuel Charge in the Engine

Ignition of the fuel charge in the solid propellant rocket engine is accomplished by an electric igniter and a pyrotechnic called the primer. The primer must create the appropriate combustion conditions in a correspondingly short time. In combustion it should provide a temperature which is higher than the ignition temperature of the propellant. In addition, the primer should provide enough pressure to exceed the minimum allowed pressure for the given fuel, at which the combustion is stable. Therefore, the primer mass  $W_p$  should be proportional to the heated surface and fulfil the inequality:

$$W_p > \frac{1}{1-\epsilon} g \frac{V_{c(1)} p_{c(p)}}{\frac{R_o}{M_{(p)}} T_p} \quad (2.2)$$

where:  $\epsilon$  = the fraction of condensed parts (solid and liquid) in the combustion products of the primer at the temperature of combustion;

$R_o$  = the gas constant;

$V_{c(1)}$  = the initial volume of the engine chamber together with the narrowing portion of the nozzle;

$p_{c(p)}$  = the pressure occurring due to the primer (this is frequently assumed to be 30-40% of the combustion pressure of the fuel);

$M_{(p)}$  = the molecular weight of the gaseous primer combustion products;

$T_p$  = the temperature of isobaric primer combustion.

In small rocket engines, with which we are frequently dealing, it is usually difficult to achieve good ignition because the ratio of inert surface metals that are heated, to the propellant combustion surface, is quite large. Colloidal fuels of the smokeless powder type usually have a lower ignition temperature, but a rather high ignition pressure is required for this. Composite-type propellants are somewhat more difficult to ignite but they do not require as high a pressure for stable combustion. A very important primer parameter is its combustion time, i.e., the time of pressure increase. M. Barrere and co-authors [7] furnished the primer combustion curves shown in Figure 2.2.

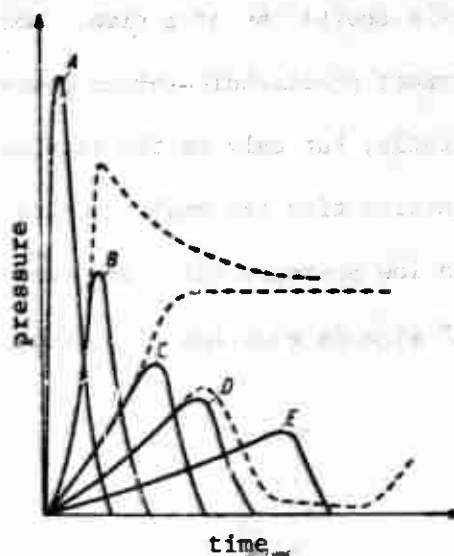


Figure 2.2. Possible curves of pressure change over time during ignition. Key: A = misfire; B = ignition with pressure peak; C = normal ignition; D = retarded ignition; E = misfire.

Ignition of the propellant surface requires time, during which a heating of the charge occurs. The heat supplied to the charge during primer combustion must exceed the heat carried away into the charge by conduction until the ignition temperature is reached. If the primer action time is very short, the heat is not able to reach the charge and because the charge does not reach ignition temperature, it does not burn in spite of the fact that the pressure far exceeds the lower pressure limit

of stable combustion of the propellant (A). The period of ignition retardation increases with decreasing pressure. The primer should assure a sufficiently rapid attainment of the pressure required for stable combustion, but without sudden jumps (C). A too abrupt ignition can give rise to a peak at the beginning of the combustion curve (B) and can even cause a rather powerful "impact", which in turn can lead to a disintegration of the (grain) charge. On the other hand, an excessively low ignition pressure when the primer action is too sluggish can be the reason for retarded ignition, unstabilized combustion or even misfire (D, E).

The burning time of the primer is regulated by reducing the size of the primer component particles or their degree of compaction. Material particles reduced to a much smaller size furnish a shorter burning time. Moreover, primers are sometimes used in the form of a compact pyrotechnic (black powder), which does not burn en masse when packed too tightly, but only on the external surface at a limited rate. In practice, the primer action time for small rockets is 10-20 msec. For larger rockets operating under a low pressure this time can be prolonged to as much as 200 msec. The "greater than" sign in equation (2.2) indicates the fact that a portion

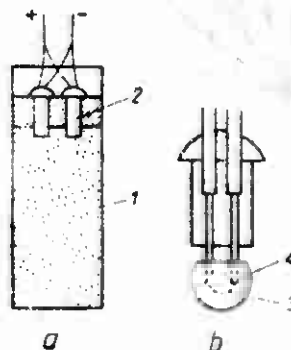


Figure 2.3. Ignition elements. Key: a = primer; b = electric igniter; 1 = pyrotechnic; 2 = electric igniter; 3 = igniter resistance wire; 4 = material mass sensitive to temperature increase.

of gases which are generated during primer combustion escapes through the nozzle before heating the charge to the point of ignition, particularly when the nozzle



opening is not initially covered; in addition, the theoretically calculated mass of the charge increases by 10-20% due to other secondary losses. The primer action is more certain if the nozzle mouth is hermetically sealed initially with a membrane, which is broken when the pressure increase reaches an appropriate value. The hermetic membrane also serves to protect the charge against the action of humidity in engines stored in the loaded state. In the case of colloidal propellant charges of the smokeless powder type, the igniter used is generally black powder; 1 kg furnishes 400 g of gaseous products with a molecular weight of 34.75, and 600 g of condensation products; the temperature of isobaric primer combustion  $T_p = 2590^\circ\text{K}$ .

Mixtures of powdered metals (Al, Mg) with oxidizing substances (perchlorates or nitrates of potassium, barium or other metals) are used as primers for other types of propellants. Primers of this type are quite frequently used in propellant research. Under conditions of actual use, they are not convenient because the finely powdered metal may be gradually oxidized during storage. Ignition of the primer pyrotechnic is accomplished by an electric igniter which consists of a charged wire and an initiator mass which is sensitive to a temperature increase (mercuric fulminate or lead azide). A typical primer and an electric igniter are shown in Figure 2.3.

In end-burning charges the primer is located at the nozzle end and in radially-burning charges it is located in the front section of the chamber, so that hot gases flow around the entire charge surface.

The casing should be durable enough so that the primer will not be spilled out and subjected to atmospheric factors, but such that it will not form fragments during combustion which could destroy the charge or plug the nozzle opening.

### 3. RHEOLOGY

We frequently encounter flow phenomena in the technological methods of producing charges, such as extrusion, molding and others, and under conditions of use of the finished charges. Sometimes the flow is an advantage (in technological cases) and sometimes a disadvantage (in the case of storing and utilization of finished charges). In addition to the flow effect in solid propellant technology, we also encounter concepts of sedimentation, castability (in composite cast propellants), brittleness, etc. When finished charges are employed, in addition to flow we also run into elastic deformation effects under the action of a widely divergent variety of stresses.

Data on the mechanical properties of propellants with specific compositions are quite scanty in the literature published to date. The only information available is generally the dependence of ballistic constants for a specific geometric shape on the mechanical properties of the propellants [7,15].

The parameters that are quantitatively capable of determining the usefulness of a propellant from a mechanical point of view are: the Young modulus, the allowable stress, the impact "strength", etc. There is no conclusive, general treatment of the mechanical properties of propellants and the effect of these properties on the internal ballistics of engines to date. Therefore, the following remarks do not pretend to provide an approach to this problem. Most solid rocket propellants are mixtures of high-molecular-weight substances (the polymer) with low-molecular-weight inorganic or organic substances. The high-molecular-weight substance (the polymer) is largely responsible for the mechanical and rheological properties of these propellants. Therefore, consideration of the mechanical and rheological properties of solid rocket propellants leads directly to a consideration of the mechanical properties of polymers.



### 3.1. Fundamental Concepts

If we axially apply an external force  $N$  to a bar with cross section  $A$  and length  $l$ , it will increase in length by the amount  $\Delta l$ .

Assuming the notations given in Figure 3.1, we have:

$\Delta l$  = the absolute elongation (in units of length),

$\epsilon = \Delta l / l$  = the relative or unitary elongation (fraction or percent),

$\sigma = N/A$  = the tensile stress, in  $\text{kg/cm}^2$ .

Similar denotations are used in the case of compression.



Figure 3.1. Stretching a bar of length  $l$  and diameter  $d$  under the effect of force  $N$ .

The relationship between these values for the stretching and compression of ideally elastic bodies is given by Hooke's law:

$$\sigma = E \epsilon . \quad (3.1)$$

The stress is directly proportional to the relative deformation (elongation, contraction), where the coefficient of proportionality  $E$  is called the modulus of elasticity. After substitution of the values  $\sigma$  and  $\epsilon$ , Hooke's law assumes the form

$$\Delta l = \frac{Nl}{EA} .$$

The bar shown in Figure 3.1 with an elongation of  $\Delta l$  will have its diameter shortened by the amount  $\Delta d$ ; thus, we have here a so-called relative transverse shortening  $\epsilon_1 = \Delta d/d$ ; the ratio  $\mu = \epsilon_1/\epsilon$  is called the Poisson number and is a constant for a given isotropic material within the limits of application of Hooke's law.

In mechanical strength calculations on elongation, the permissible elongation stress is assumed to be  $k_r$  for the given material, whereby:

- (a) the following equation is used in verifying the stresses

$$\sigma_{max} = \frac{N}{A} \leq k_r \quad (3.2)$$

- (b) in determining the cross section

$$A \geq \frac{N}{k_r} \quad (3.3)$$

- (c) in calculating the permissible tensile force

$$N \leq Ak_r \quad (3.4)$$

These same equations are used in the case of contraction, except that the permissible contraction stress is assumed to be  $k_c$  instead of  $k_r$ . As is well-known, there are no ideally elastic bodies; therefore, the validity of Hooke's law for all solid bodies is limited to a certain, rather narrow range of stresses and deformations. A typical stress-deformation dependency curve for an actual (not ideal) solid body is shown in Figure 3.2, where  $R_H$  denotes the limit of proportionality

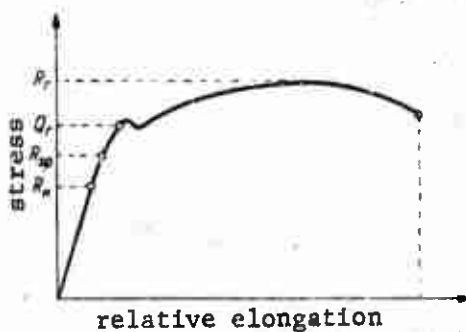


Figure 3.2. A typical curve showing the dependence of deformation on stress in the elongation of a bar.

(this is the ratio of this force to the cross section  $A_0$  -- the primary cross

section of the sample -- above which Hooke's law ceases to be applicable when elongation occurs);  $R_{sp}$  -- the conventional elasticity limit (this is the ratio of the force to the cross section  $A_0$ , whereby the stable deformations do not exceed a certain conventional value);  $Q_T$  is the physical limit of plasticity (the ratio of this force to the cross section  $A_0$ , whereby the sample is deformed without a distinct increase in loading). The so-called limit of conventional plasticity (in contrast to the physical limit) is defined for materials which do not exhibit a definite plasticity limit; this is the ratio of the force to the cross section  $A_0$ , corresponding to a stable deformation, e.g., of 0.2%.  $R_T$  denotes the tensile strength (this is the ratio of the greatest tensile force exerted on the sample during elongation of the cross section  $A_0$ ).

The important parameters in studies on rupture are still the total stable elongation after rupture

$$a_p = \frac{l_1 - l_0}{l_0} 100\%$$

and contraction at the site of rupture of the sample

$$c = \frac{A_0 - A_1}{A_0} 100\%$$

Studies on the impact strength of materials constitutes another type of research. This is a test of the dynamic bending of a sample of definite dimensions, with or without a notch, by striking it with a special pendulous hammer, which falls from a definite height. If we assume that  $L$  is the work used to break the sample in  $\text{kgm}$  and  $A$  is the cross-sectional area of the sample at the site of rupture in  $\text{cm}^2$ , the following ratio is then called the impact strength:

$$U = \frac{L}{A} [\text{kgm}/\text{cm}^2] . \quad (3.5)$$

The compression, tensile and impact strength tests are the main studies carried

out in determining the mechanical properties of solid bodies. The shear effect will be discussed in connection with the flow which appears in plastic deformations. Studies such as the bending effect, investigation of the resistance to fatigue or torsion, are considered among special studies of materials. The mechanical and rheological properties of materials change with variations in temperature. These changes are more evident in nonmetallic substances, such as polymers.

As a function of the temperature, a polymer can be made similar in its properties to one of 3 substance types, each of which exists separately in an ideal form. They are:

- (1) a Newtonian fluid, the viscosity of which is not a function of the flow rate;
- (2) an ideally elastic body, subject to Hooke's law, the small reversible deformations of which are directly proportional to the stresses applied (solid materials below the temperature of brittleness are similar to such bodies);
- (3) an ideal elastomer, which is capable of reversible deformations of several hundred percent and which has considerably less strength and modulus than an ideally elastic body.

In practice, however, a polymer almost always has features of all 3 types of substances. Therefore, it is a rather complicated matter to determine the relationships between the stresses and the resultant deformations, the temperature, time and other variables.

The theories which have been advanced up to now on the mechanical properties of materials and which embrace all the relationships in mathematical equations have the disadvantage that they offer no physical interpretation for the effect, i.e., none of the theories explain in a molecular manner the theory of the 3 basic rheological conditions: elasticity, flexibility and fluidity. According to some authors [26, 28], these 3 properties of polymers are explained by the following molecular mechanisms:

- (1) a reversible stretching of the bonds and a deformation of the angles

between the bonds of the basic polymer chain determine the elasticity which occurs under instantaneous loads;

(2) reversible straightenings of the polymer chains determine the flexibility;

(3) an irreversible shifting of the chains in relation to each other determines the capacity for stable deformations (flow or yield).

If we assume that the initial state is a fluid state conforming to the Newtonian fluid laws, in the physical sense it is either a specific liquid or a solid body capable of flow. Flow or yield is always characterized by the displacement of layers of the material in the direction of the applied stress. Therefore, this effect can be embraced in the equation which determines the shear [28].

If the force is tangent to the deformations, as in Figure 3.3, then we determine the deformation as a function of the tangential stresses

$$\gamma = \frac{dx}{dy}$$

The rate of flow is determined by

$$D = \frac{d\gamma_p}{dt}$$

where  $\gamma_p$  is the stable deformation.

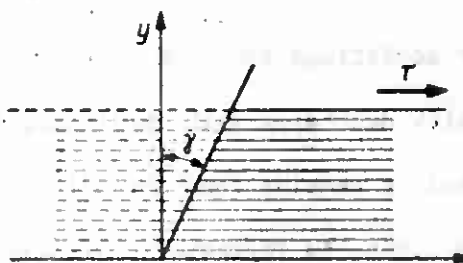


Figure 3.3. Deformation under the influence of shear forces

For a Newtonian fluid the rate of flow is proportional to the applied stress



$$\tau = \eta \cdot D$$

(3.6)

In this case the viscosity of the liquid  $\eta$  is a constant, independent of the rate of flow  $D$ .

Most fluids have this property (Figure 3.4a). Thus, for example, all monomers, some polyester resins before hardening, diluted polymer solutions and other fluids employed in propellant technology conform to Newton's law. On the other hand, concentrated polymer solutions, low-molecular-weight polymers and monomers with a large amount of solids in suspension, which we also encounter in solid rocket propellant technology, do not conform to Newton's law.

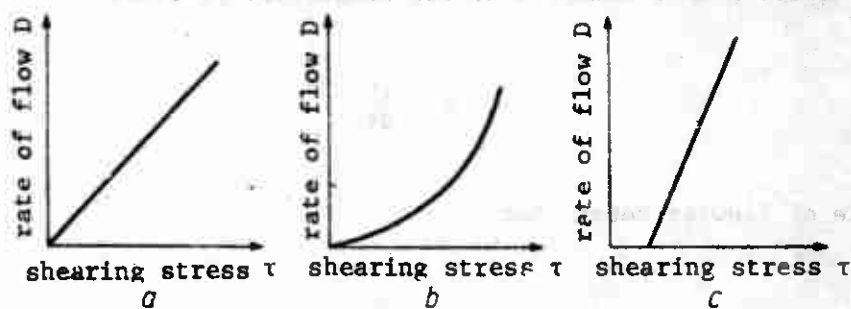


Figure 3.4. Basic curves showing the dependency of flow rate on stress. Key: a = a Newtonian fluid; b = a fluid with a pseudoflow zone; c = a fluid having a flow point.

There are 2 types of deviations from the model of a Newtonian fluid. In the first of these the viscosity decreases with increasing flow rate  $D$  (Figure 3.4b). Quite frequently the viscosity remains constant after reaching a certain minimum value as the flow rate continues to increase (coefficient of viscosity). In this case the dependence of the flow rate on the loading is not rectilinear in the beginning but then becomes so after reaching a certain maximum loading. Then it is often said that the substance has a zone of pseudoflow or pseudoplastic flow (the flow rate increase is not proportional to the loading) and a zone of Newtonian flow.

The pseudoflow effect is closely associated with another type of deviation

from a Newtonian fluid, characterized in Figure 3.4c. In this case the flow begins only after the stresses have increased to a certain point. Most frequently, substances having this stress limit do not flow like Newtonian fluids after this limit is reached but have a pseudoflow zone; this boundary is often called the plasticity boundary. The concept of the plasticity boundary determined in this manner is analogous to the concept of the plasticity boundary determined at the outset of this section. The difference lies only in the approach to the problem.

Formerly, the concept of the plasticity boundary was determined by working from ideally elastic bodies; in more recent deliberations this value was determined by working from an "ideal fluid" (a Newtonian fluid). This treatment of the problem is particularly apt if we are considering the mechanical and rheological properties of plastics because these substances, like all high-molecular-weight substances, combine the properties of solids and liquids. If the most important characteristic for solids is the modulus of elasticity, and viscosity is the most important for liquids, these 2 characteristics are simultaneously germane in the case of high-molecular-weight substances. In both cases we are dealing with the deformation of substances under the effect of applied stresses, except that in the case of liquids, in contrast to solids, this deformation is irreversible and is a function of time. Therefore, when we consider the problem in time, we find that any liquid subjected to the action of a force for an infinitesimally short time exhibits a distinct elasticity, and conversely, any real solid subjected to the action of forces for an infinitely long time exhibits flow effects. Hence, it can be specifically deduced that in practice there are no ideally elastic substances nor perfect liquids, and this division is a matter of convention to a certain degree. However, it is justified by the fact that in the range of possible experimentation almost every real substance exhibits a distinct preponderance either for elastic or for plastic characteristics. Only high-molecular-weight substances modified in different manners are capable of possessing both elasticity and plasticity to the same degree.

One other type of flow is less frequently encountered, namely, dilatation flow,



in which the viscosity of the material increases with increasing shearing rate.

Non-Newtonian flow can be mathematically represented by the equation

$$\frac{dy}{dt} = B\tau^n \quad (3.7)$$

where B and n are constants for the given material and can be determined for each material from experimental data on the dependency curve: the logarithm of the shearing rate versus the logarithm of the shearing stress. For Newtonian liquids,  $n = 1$  and  $B = 1/\eta$ .

Quite frequently, mixtures of Newtonian or non-Newtonian fluids with powdered solids are also used in the exploitation and technology of solid propellants. The rheological characteristic of such mixtures is usually the existence of plasticity boundaries (Figure 3.4c); after these limits are passed the substance may flow like a liquid or like a pseudoplastic substance.

There are also certain mathematical relationships, according to which the viscosity of the suspension at a given flow rate can be calculated from the viscosity of the liquid itself. One of these relationships is the equation derived by Guth and Simh:

$$\eta = \eta_0 (1 + 2,5\phi + 14,1\phi^2) \quad (3.8)$$

where:  $\eta$  = the viscosity of the suspension;

$\eta_0$  = the viscosity of the pure liquid,

$\phi$  = the volume fraction of the powdered (dispersed) phase.

This equation is valid for more highly concentrated suspensions, with which we are frequently dealing in solid propellant technology. However, it should be borne in mind that in practice certain deviations from the above relationship can occur. These deviations are caused by the symmetry of the particles (the relationship is valid for spherical solid particles), solvation and swelling of the particles, and a different wettability of the particles of the diffused phase by the liquid.

If we are dealing with pure polymers (without fillers) having a plasticity limit, there are certain theories associating this property with their molecular structure. One of these is the theory which introduces the concept of the activation energy of flow. In "fluids" having a flow limit, the movements of the molecules are quite limited and in order to maintain this molecular movement, which is necessary for viscous flow, a certain amount of energy  $E$  must be supplied. This energy is called the activation energy of flow in the case of polymers. This value appears in the following equation for the dependency of viscosity on temperature:

$$\eta = Ae^{E/RT} \quad (3.9)$$

The activation energy value increases with increasing molecular weight, but not proportionally to the temperature of vaporization. After reaching a certain

TABLE 3 1. THE BASIC MECHANICAL PROPERTIES OF SOLID PROPELLANTS

Name of the physico-mechanical property	For propellants		For steel
	colloidal	composite	
Modulus of elasticity kg/cm <sup>2</sup>	1,000-3,000 (20°C) 200-1,000 (50°C)	1,000-2,000 (-40°C) 100-200 (+15°C) 50-100 (+40°C)	$2.1 \cdot 10^5$ (15°C)
Poisson's ratio	0.35-0.50	0.35-0.50	0.30
Coefficient of linear heat expansion, 1/°K	$1.2 \cdot 10^{-4}$ - $2.0 \cdot 10^{-4}$	$0.5 \cdot 10^{-4}$ - $1.5 \cdot 10^{-4}$	$1.2 \cdot 10^{-5}$
Specific heat, kcal/kg°K	0.35	0.30	0.11
Coefficient of heat conduction, kcal/sec cm °K	$0.50 \cdot 10^{-6}$ - $0.53 \cdot 10^{-6}$	$0.7 \cdot 10^{-6}$ - $0.75 \cdot 10^{-6}$	$1.1 \cdot 10^{-4}$
Coefficient of heat diffusion, cm <sup>2</sup> /sec	$0.215 \cdot 10^{-4}$	$0.30 \cdot 10^{-4}$ - $0.30 \cdot 10^{-4}$	$0.31 \cdot 10^{-2}$

maximum activation energy value, this value remains constant with a further increase in the molecular weight. It is thus deduced that in the case of molecules with a

very long chain, the element that is displaced during flow is not the whole molecule, but only a certain portion of it. Thus, the activation energy increases to the point where the molecular weight does not exceed to a significant degree the size of the segments that are being displaced. As the temperature of the material is lowered, the micromovements (of particle fragments) and macromovements (of whole particles) are restricted and at a certain temperature they are generally inhibited. Then the substance changes from a plastic-elastic state to a glassy-brittle one and can be treated as a frozen liquid.

The temperature of brittleness is sometimes defined as the temperature of the second order transformation; of course, the latter involves the same effect, but it is defined on the basis of entirely different parameters and therefore can frequently differ quantitatively from the temperature of brittleness, which is usually higher [28].

The temperature of brittleness of a substance depends on such factors as: the molecular weight, second order bonds (polar, hydrogen), transverse bonds, molecular flexibility, the plasticization factor, filler, and degree of polymer crystallization. The temperature of brittleness changes (decreases) with increasing molecular weight until the molecular weight exceeds a value of about  $10^4$ ; above this value, it is constant. The temperature of brittleness is higher with the appearance of transverse bonds. Bonds of the second order, which have a particularly high bonding energy in the case of polymers with strongly polar groups, exert a distinct influence on this temperature (Table 3.2). Like the polar groups, the ordinary hydrocarbon branches from the main chain also reduce the flexibility of the particles, which leads to an increase in the temperature of brittleness. The flexibility of the molecules usually increases when there are double bonds in the chain.

The mobility of the particles can be increased by moving them apart, whereby they cease to act on each other. The role of diluent for the molecules is played by plasticizing substances: dibutyl phthalate, dioctyl phthalate, tricresyl phosphate and many others, mainly esters of bi-functional acids with higher alcohols or

multi-functional alcohols with higher acids.

In addition to "external" plasticization, "internal" plasticization can take place by incorporating the molecules of another polymer with a lower temperature of brittleness in the chains of the given polymer. The plasticization of polystyrene by copolymerization with butadiene can be cited as an example of this. In this manner the aromatic rings which inhibit the movement of the polystyrene molecules are separated from each other and the double bonds arising from the butadiene further plasticize the copolymer, which becomes rubber-like. Most fillers generally have little or no effect on the temperature of brittleness. Some substances are in the brittle-glassy state at normal temperatures; on the other hand, normal temperature (20°C) is higher than the temperature of brittleness for some (Table 3.2).

It follows from studies that have been carried out that high-molecular-weight substances are mostly viscous-elastic substances from a rheological point of view, in which viscous flow and elasticity dominate the picture or recede, depending on the nature of the substance and the temperature.

As already stated, elastomers have a special position among the very numerous high-molecular-weight substances. Their differentiation is not conditional on qualitatively different properties but only on a quantitative expression of the already mentioned properties. Therefore, the elastomers are all numbered among the viscous-elastic substances. However, this is a subgroup of substances that are characterized, in contrast to other elastic substances, by a capacity for elastic deformation amounting to several hundred and even a thousand percent, which disappears when the stresses are removed. All the theories that have hitherto been offered in explanation of the elasticity effect lead to the statement that elastomer molecules are rolled in coils and balls, which straighten out when stresses are applied.

All the types of substances considered enter into the technology and utilization of solid propellants; and consequently, a knowledge of the laws governing these substances is absolutely necessary in the selection of optimal technological or practical indications.

TABLE 3.2. THE BASIC MECHANICAL PROPERTIES OF TYPICAL SYNTHETIC MATERIALS

No.	Polymer	$R_r$ [kg/cm <sup>2</sup> ]	$E$ [%]	Modulus of elasticity [kg/cm <sup>2</sup> ]		Impact strength without notch* [kg/cm <sup>2</sup> ]	Temperature of brittle- ness [°C]
				initial	with 300% extension		
	<u>Vinyl-like</u>						
1	Styrene	400	1-4	$1-4 \cdot 10^4$	-	20	80
2	Ethylene	100-200	200-750	$1 \cdot 10^3$	-	-	-68
3	Vinyl chloride	600	-	$4.5-9 \cdot 10^4$	-	100	80
4	Plasticized vinyl chloride	300-500	10-40	$1-2 \cdot 10^4$	-	-	-20
5	Methyl methacrylate (cast)	400-700	1-10	$2-4 \cdot 10^4$	-	20	70
	<u>Cellulose-like and others</u>						
6	Cellulose acetate	200-600	7-80	$1-3 \cdot 10^4$	-	25	
7	Cellulose aceto-butyrate	200-500	50-70	$1-2 \cdot 10^4$	-	-	
8	Benzyl-cellulose	400	5-30	$25 \cdot 10^4$	-	-	
9	Phenyl-formaldehyde polymer	450	1.0-1.5	$5-7 \cdot 10^4$	-	5	
10	Cellulose nitrate + 27% plasticizer	600				150	
	<u>Rubber-like polymers</u>						
11	Natural crude rubber	20-40	800-120	-	5-10	-	-60

\* In accordance with German research methods VDE 0320

TABLE 3.2. (continued)

No.	Polymer	$R_r$ [kg/cm <sup>2</sup> ]	E [%]	Modulus of elasticity [kg/cm <sup>2</sup> ]		Impact strength without notch* [kg/cm <sup>2</sup> ]	Temperature of brittle- ness [°C]
				initial	with 300% extension		
12	Natural vulcanized rubber	275-350	675-850	10-20	11-24	-	-55
13	Natural vulcanized rubber (80% kaolin + zinc white)	60-90	250-400	55-70	40-75	-	-42
14	Vulcanized butadiene-styrene	30-60	300-450	10-30	10-50	-	-58
15	Vulcanized butadiene-styrene (30% carbon black + 10% softener plasticizer)	200-250	400-750	25-45	30-115	-	-58
16	Vulcanized chloroprene (20% carbon black)	250-310	550-760	30-50	45-75	-	-40
17	Diethyl ether multisulfide (thiokol B), vulcanized, (25% carbon black)	35-55	200-300	40-60	45	-	Thiokol F-35

\* In accordance with German research methods VDE 0320



Rheological and mechanical problems will be discussed further in subsequent sections of this book. A more thorough treatment of these problems can be found in a number of foreign and domestic publications.

### 3.2. Mechanical and Rheological Indices of Prepared Fuels

Previous studies and publications indicate that the usefulness of a propellant from a mechanical standpoint can only be determined by a whole series of experiments. The literature contains [15,7] definite data concerning what is required of polymers for given geometric shapes of the charge. These requirements are very diverse because different stresses arise with each geometric charge configuration. The deformations caused by stresses in different geometrical configurations affect the ballistic parameters of the engine differently. Thus, the problem of the mechanical parameters of a propellant has meaning only with reference to a specific configuration. Generally speaking, solid propellants can be rigid and brittle or soft and elastic [17]. Rigid propellants are usually more suitable for charges which are inserted freely into the chamber, while elastic propellants are indispensable in the preparation of charges which are made to adhere to the chamber walls.

The properties of a propellant vary with the temperature, as do the properties of a polymer. M. Barrere gives the breaking strength of a certain composite propellant as a function of the temperature (Figure 3.5).

It is evident from the graph that this propellant can be either too soft or too hard and brittle at extremely different ambient temperatures and that the material abruptly changes its plastic-elastic properties at a temperature of about  $-25^{\circ}\text{C}$ ; at this temperature the elastic elongation decreases to a minimum and the plastic deformation generally disappears. Moreover, composite fuels, being a mixture of a crystalline oxidizer and a polymer, change their properties in accordance with the mutual change in polymer and oxidizer reaction below the temperature of brittleness. This leads to the formation in the propellant of internal micro-stresses and occasionally to micro-cracks around individual oxidizer crystals, so that the appearance



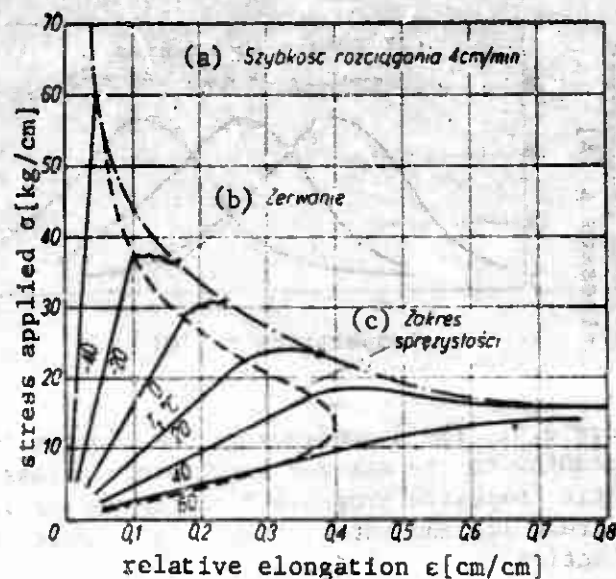


Figure 3.5. The elastic tension curves of a composite propellant, composed of a mixture of finely powdered oxidizing substance and a polymer combustible component (binder). Key: (a) = extension rate, 4 cm/min; (b) = rupture; and (c) elasticity range.

of the samples assumes a dull hue due to the appearance of micropores. The loading action rate also influences the mechanical-rheological properties (Figure 3.6).

It follows from the curves in the diagram that the very rapid loading induced by ignition is very dangerous at low temperatures; even for very elastic propellants (elongation of about 50%). The danger lies in the fact that the propellant behaves as a brittle mass, for which the stresses arising can exceed the permissible stresses and a cracking of the charge may occur. It follows from this that a polymer which is a brittle substance under the actual conditions in the rocket ( $-40, +50^{\circ}\text{C}$ ) cannot be used as a binder for composite-type propellants. Almost all polymers are unsuitable for these purposes below the temperature of brittleness because their permissible stresses (with a considerably reduced crystalline oxidizer content) are lower than the stresses which arise during operation of the engine. Thus, it is necessary to use either plastic-elastic polymers which have a temperature of brittleness below  $-40^{\circ}\text{C}$ , or plasticized polymers in a pure brittle form. When

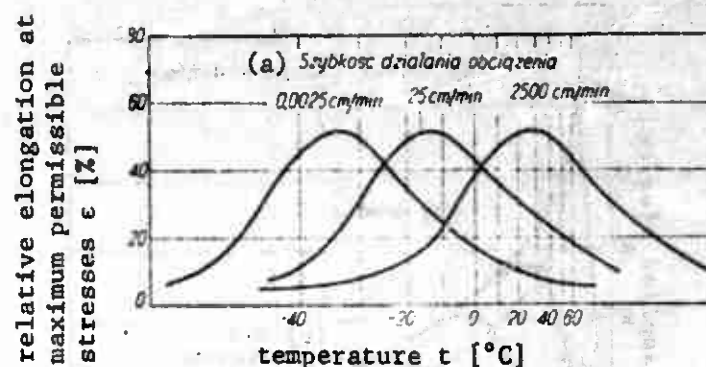
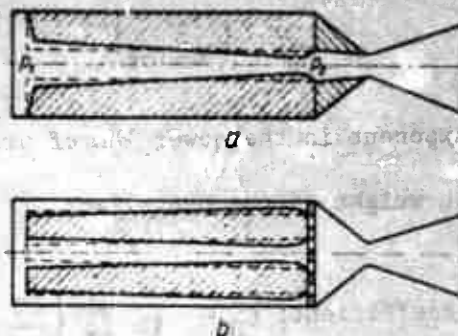


Figure 3.6. The dependency of the elongations corresponding to the maximum permissible stress in an elastic composite propellant on the temperature at different loading rates. Key: (a) = rate of loading action.

proceeding in the direction of plasticization and elasticization, it is also necessary to take precautionary measures so that an excessively great deformation does not occur under the effect of the stresses that arise. Most of the data published to date define the permissible limits of softening of the propellants. These limits are dictated by changes in the ballistic characteristics of the engine arising from deformations of the powder charge. Such deformations can occur in charges of large dimensions during storage or combustion due to forces arising in the burning process and the flight of the engine. The most typical deformations of a powder charge composed of soft material are illustrated in Figure 3.7.

Such deformations of the charge decrease the free flow cross section  $A_p$ , which in turn causes an increase in the pressure difference between the front and back sections of the chamber. The increase in this difference induces a more rapid gas flow, permissible only to a certain boundary velocity, above which this velocity causes erosive combustion.

The appearance of erosive combustion increases the total burning rate; then the pressure increases, and the engine may blow up. In order to foresee all these changes, it is necessary to know what forces act on the charge. By disregarding the frictional force and the impact of the gases on the possible transverse projections



---- charge before deformation  
 ——— deformed charge

Figure 3.7. Deformation of a powder charge under the effect of forces acting in the engine: a = a charge attached to the chamber wall, b = a cylindrical charge in a free (unattached) state.

of the charge, the longitudinal stresses acting on the charge can be calculated by means of the equation

$$\sigma_z = p_1 - p_2 + L \rho_p j \quad (3.10)$$

where:  $L$  = the charge length,  
 $j$  = the longitudinal acceleration of the rocket,  
 $\rho_p$  = the propellant density,  
 $p_1$  and  $p_2$  = the pressure in the combustion chamber (Figure 3.7).

The difference  $p_1 - p_2$  is calculated from the known, approximate internal ballistics equation [7,31]

$$\frac{p_1 - p_2}{p_1} = k \left( \frac{2}{k+1} \right)^{\frac{k+1}{k-1}} \left( \frac{A_{cr}}{A_p} \right)^2$$

where  $k$  = the adiabatic exponent ( $k = c_p/c_v$ ) of the products;

$p_1$  can be approximately determined with the equation

$$p_1 = \left( \frac{A_p \gamma_p a}{C_D \cdot l_{cr}} \right)^{\frac{1}{1-a}}$$

where:  $n$  = the power exponent in the power law of propellant combustion,

$\gamma_p$  = the specific weight of the propellant,

$C_D$  = the output coefficient;  $C_D = \sqrt{\frac{gk}{RT_0} \left( \frac{2}{k+1} \right)^{\frac{k+1}{2(k-1)}}}$

$a$  = the coefficient in the burning rate equation:

$$r = ap^n$$

It is evident from the above that the magnitude of the stresses generated can be varied by varying the geometrical configuration of the charge ( $A_{sp}$ ,  $A_p$ ). The maximum stresses arise at the beginning of combustion (when  $A_{sp}/A_p$  has its maximum value), when the pressure difference in the front and back portions of the chamber is critical. However, the stresses which arise later from the inertia of the engine and the acceleration in time of the flight play an important role.

There is a definite mathematical dependency [7,31] of the modulus of elasticity on the value

$$J = \frac{K_I}{K_n} = \frac{A_{cr}}{A_p}$$

When other data on the propellant and the rocket are known, it is possible to determine the minimum moduli of elasticity for the nominal values of the  $J$  ratio on the basis of this dependency. The changes in the  $J$  ratio (due to charge deformations) as a function of the modulus of elasticity are illustrated in Figure 3.8.

The portion of the curve lying above point M corresponds to unstable combustion, in which the charge deformation is so great and progresses so rapidly that it exceeds the increase in output of the gases flowing through the free cross-sectional

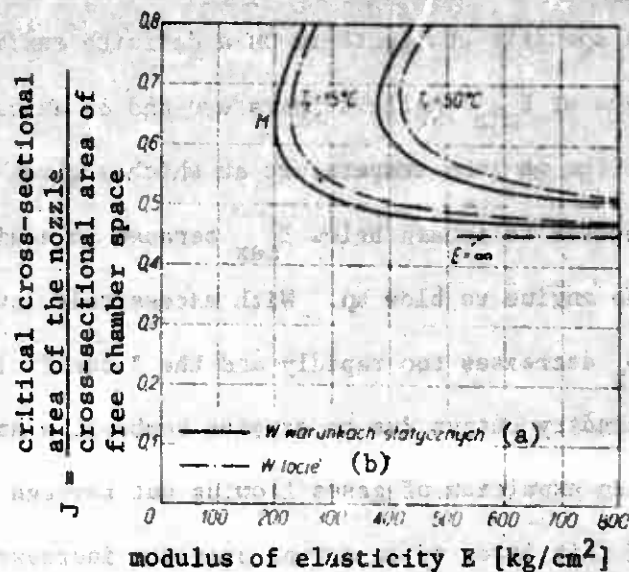


Figure 3.8. The dependence of the J property on the value of the elasticity modulus of a cylindrical charge in a detached state. Key: (a) = under static conditions; (b) = during flight.

surface area.

If the propellant has a large modulus of elasticity, its deformation will be slight; thus, the charge will change scarcely at all. Therefore, in this case it is sufficient for a good functioning of the propellant if the stresses formed do not exceed the magnitude of destructive stresses. However, as previously stated, the magnitude of destructive stresses in rigid propellants is low (the charge may crumble); therefore, it is better to work with propellants with a smaller modulus, which do exhibit a greater deformation under the stresses encountered. On the other hand, as shown in the graph, there is a definite  $E_{\min}$  value; if

$$\frac{dJ}{dE} = \infty,$$

$E_{\min}$  increases with increasing initial temperature of the charge. It is evident from Figure 3.8 that if  $E_{\min} = 200$  for  $15^{\circ}\text{C}$ ,  $E_{\min} = 400$  for  $50^{\circ}\text{C}$ .

Taking into consideration the fact that the actual modulus (that possessed by



the material) decreases with increasing temperature, we see that for each specific substance and for a specific charge there is a definite maximum temperature at which the dependency curves of  $E_{\min}$  on the temperature and of actual  $E$  on the temperature intersect. This is the maximum temperature at which a given charge can be burned. In practice it is better to remain below  $T_{\max}$  because an accidental pressure increase can cause the engine to blow up. With excessively low modulus values, the free flow surface  $A_p$  decreases too rapidly and the  $J$  coefficient increases. Then the increase in secondary output due to erosive combustion and pressure increase exceeds the increase in expulsion of gases flowing out through the free cross-sectional surface area and this leads to an abrupt pressure increase and blow-up of the chamber. W. Kozakiewicz [30] in his book gives the dependency curve of stresses generated in the charge on the  $J$  and  $K_n$  ratio, in accordance with Berfley and Mills. It is evident from the graphs presented in that book that for constant  $J$ , the stress values are different for different  $K_n$  values. For example:

when  $J = 0.6$  and  $K_n = 100$ ,  $\sigma = 4 \text{ kg/cm}^2$ ,

if when  $K_n = 190$ ,  $\sigma = 25 \text{ kg/cm}^2$ .

In calculating the stresses generated in a charge using equation (3.10), the frictional forces, which according to Wimpres [15] are of the same order toward the end of burning of the charge as the forces resulting from the pressure difference, are not taken into account. The thermal stresses that arise in any charge during temperature changes have not been taken into account up to this point. It is evident from the studies by Barrere [7] that particularly large thermal stresses are generated in charges which adhere to the chamber walls. Therefore, in the case of charges which adhere to the chamber walls it is absolutely imperative to select soft and elastic propellants that have a low temperature of brittleness and a low modulus of elasticity.

In general, it should be stated that assurance of the required charge strength constitutes a very complex problem inasmuch as it is difficult to foresee all the

parameters upon which the charge strength depends when it is designed. Therefore, it is better to rely on experimental data in formulating a charge from a specific propellant substance. In any case, Tables 3.1 and 3.2 give the mechanical properties and moduli of elasticity for propellants of the composite and colloidal types and for individual plastics; this can be of help in the choice of appropriate substances for combustible binder substances.

The modulus of elasticity of composite propellants in current use is  $10^3$ - $10^5$  times less than the modulus of elasticity of steel. A comparison (according to Barrere) of the principal mechanical and physical properties of nitroglycerin powder-type propellants, composite fuels and steel is given in Table 3.1. It is evident from this comparison that other propellant properties are also some scores of times less than steel in more than one case, e.g., all the heat-thermal properties of powders. The figures cited explain why powders that adhere to the chamber walls function so poorly and elucidates the need for the powder mass to be very elastic under all temperatures encountered in use in the case of charges that adhere to the walls. A powder propellant would be subjected to cracking and detachment at minimal temperature fluctuations with at least a tenfold greater linear thermal expansion. It follows from a comparison of the elasticity moduli of polymers and existing powders that the moduli of polymers are about 10 times larger than the moduli of the propellants used. It is evident from Table 3.2 that the elasticity moduli of common vinyl (with the exception of polyethylene) and cellulose derivative polymers exceed the value of  $1 \cdot 10^4$ . In addition, the temperature of brittleness for vinyl substances, with the exception of polyethylene, is much higher than normal. Accordingly, pure (not plasticized) vinyl or cellulose substances are not suitable as rocket propellant constituents because of their mechanical properties. It is possible to use them only in the plasticized form, in which there is a lowering of the modulus of elasticity and the temperature of brittleness, as evinced by the example of polyvinyl chloride. Following the employment of plasticizers, substances such as cellulose nitrate in the form of a colloidal fuel can be used in the manufacture of



rocket propellant charges.

Rubbery materials, whose temperature of brittleness is low and which have an elasticity modulus very close to that required, are much more suitable in propellant manufacture because of their mechanical properties. The modulus of elasticity in rubber-like substances has a value which is somewhat below that required even though it considerably exceeds the upper limit (Table 3.1 and Figure 3.7) in vinyl and cellulose substances. However, as can be seen in Table 3.2, the modulus value undergoes a distinct increase with vulcanization and the employment of a filler. When it is remembered that the filler in composite fuels is about 70-80%, it can be seen that the modulus of elasticity will be raised to the desired value in the finished propellant. All the requirements mentioned with respect to the modulus of elasticity refer to charges burning on the lateral surface. Propellants with predominantly plastic properties can be used for end-burning charges.

### 3.3. Rheology and Sedimentation Effects Associated with Propellant Technology

Propellant charge technology bears a great deal of similarity to the technology of plastic products. The principal methods of manufacturing articles from synthetic substances are: compression molding, extrusion molding and casting. In each of these methods the technician is confronted by a whole complex of problems, which become even further compounded in the case of propellant charge manufacture. One of the factors complicating the technology of propellant charge processes is the fact that the high temperatures employed in the production of plastics are not permissible here. For example, in ordinary compression molding a temperature of  $150^{\circ}\text{C}$  and a pressure of  $70\text{--}220\text{ kg/cm}^2$  are used, while in the case of the so-called injection molding, the temperature is above  $250^{\circ}\text{C}$  and the pressure is  $700\text{--}2100\text{ kg/cm}^2$ . Temperatures this high assure complete fluidity of the formed mass, which fills the form completely and eliminates air bubbles. However, at such high temperatures some solid propellant components tend to decompose, which can lead to spontaneous ignition and an explosion.

### 3.3.1. Compression molding

As numerous studies on the compression molding of solid polymers with fillers at low temperatures demonstrate, compression molding cannot assure the desired product quality if the binder does not attain a state of fluidity. Union of the polymer with the filler, which consists of crystals of an oxidizing substance in the case of composite fuels, is inadequate; in addition to the basic components, air is entrapped and weakens the whole product through the formation of interstitial micropores. When such propellant charges are burned, the charge disintegrates and the engine blows up. Thus, it is obvious that this method cannot be widely used in the production of composite-type propellant charges. This method can be employed only for charges of small dimension, molded with a somewhat plasticized binder, and in the case of propellants burning under low pressure. An example of such propellants can be low-energy composite fuels of substoichiometric composition, which are widely used in rocket models (not full scale). In this case combustion takes place under a very low pressure and with a deficiency of oxygen; then the combustion products do not enter the micropores although the combustion is very intense on the exposed area.

### 3.3.2. Extrusion molding

In the production of charges from colloidal and some composite fuels, it is more suitable to use the extrusion method, which can be considered a variant of compression molding. This method has long been used in the production of artillery explosives (powders) and is described in the work by T. Urbanski [33].

The propellant mass must be capable of flowing under pressure if this method is to be adapted for charge production. Almost all polymers fulfil this requirement after appropriate plasticization or heating. In the case of colloidal fuels, the plasticizer is one of the principal constituents of the propellant, nitroglycerin. From the point of view of facilitating the processing, it is desirable to add a

large amount of plasticizer; on the other hand, as is well-known from utilization requirements, the charge cannot be too plastic. The principal requirement of the plasticizing substance is an ability to dissolve the polymer so that a homogeneous gel is obtained, whose composition does not change in time because of a lack of ability to "sweat" and evaporate under utilization and storage conditions. With respect to evaporation, this condition is fulfilled if the plasticizer has a low vapor pressure and if it is distinguished by a low rate of diffusion in the polymer. Both of these conditions are fulfilled by substances with a high molecular weight. The most frequently used plasticizers are esters of high-molecular-weight acids; sometimes, certain ketones, amides, nitriles, sulfoamides and, in some cases, low-molecular-weight polymers are used as plasticizers. Hitherto, the choice of a plasticizer has been guided chiefly by experimental results, without theoretical premises.

The disadvantage of the extrusion method is the necessity of using rather large presses, the size of which is proportional to the size of the extruded charge. Bearing in mind the tendency to produce larger and larger charge diameters (up to as much as several meters), this method has many opponents. Nevertheless, this method is currently used for charges of average size, which indicates that it must not be disregarded altogether. Extruded charges can be larger in the case of more fluid masses. Therefore, charges of considerable diameter can be obtained by this method from substances which are plastic during the formation process and then become rigid after formation.

Composite fuels based on elastomers as the combustible component, which are being used more and more at the present time, conform to this condition. Butadiene-styrene rubbers, natural rubber, polysulfide rubbers and polyurethans are frequently used as elastomers in this case.

Extrusion of a propellant based on these elastomers takes place before vulcanization or before the final hardening of the polymer. Consequently, extrusion molding can be carried out at cold temperatures and at comparatively low pressures.

Previously, piston extruding presses, which operate in a periodic manner, were

most frequently used in the technology of smokeless powders. Before loading into the cylinder of the extruding press, the masa must be given a final mixing and be plasticized; this is performed in the so-called kneading machines. Then the mass is charged into the cylinder of the extruding press in such a manner that the air content in the mass is reduced to a minimum. Each end of the cylinder is closed with a molding head; the cylinder may be heated or cooled. A diagram of the piston extruding press is given in Figure 3.9

In the molding head opening a core which shapes the appropriate opening in the extruded form can be placed on the grid.

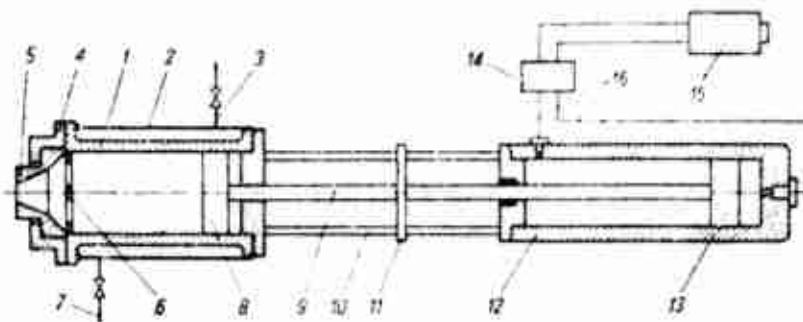


Figure 3.9. Diagram of a piston extruding press: 1 = cylinder, 2 = heating jacket arrangement, 3 = heating medium inlet, 4 = head housing, 5 = holding head, 6 = grid, 7 = heating medium outlet, 8 = piston, 9 = piston rod, 10 = guide bar, 11 = yoke, 12 = hydraulic cylinder, 13 = piston, 14 = manipulator, 15 = pump, 16 = oil pipes.

A more modern method of formation is the so-called "sznekowanie (screw feed conveyor)". This is a combination of extrusion or compression molding with a continuous (non-periodic) feeding of the mass. The mass is fed by means of a worm conveyor, at the end of which there is a molding head or die, toward which the material is pressed. Arrangements of this type are often called screw presses, screw machines or simply screws. The most correct terms in Polish nomenclature are worm extruding press or worm press. In addition to the continuity of the process, worm extruding presses are advantageous because as the worm turns, it not only forces the mass forward, but also exerts a thorough mixing and plasticizing action on it.

Compression molding in this type of apparatus has been used for quite some time for the manufacture of war materials in the preparation of artillery shells containing explosive materials. Worm extruding presses have previously been used principally in the technology of plastics and rubbers, in the cable industry, etc. In recent years, references in the literature to new technological processes for solid propellants [7] and the rapid introduction in industry of new and improved types of worm extrusion presses point to the possibility of an increasingly widespread adaptation of these machines to the production of solid propellant charges.

Worm extruding presses can be divided into 2 basic types: single-worm and multi-worm. Each of these basic types can embrace extruding presses for different purposes, and in this connection they can have different heating or cooling systems, ventilation systems, etc. The single-worm extruding press has some systems identical to the piston extruding press. Worm extruding presses have a worm instead of a piston in the cylinder. For all practical purposes, the length of the worm is approximately equal to fifteen times its diameter, although this ratio is considerably larger in some newer extruding press types. The charging hopper is located above the worm, at its rear section. The mass is taken up from here by the revolving worm, and then moved forward toward the molding head or die by the revolving worm. Depending on its length, the cylinder is usually divided into several zones, each separately heated or cooled. Cooling may also take place via the core of the worm. In some extruding presses a degassing system connected to a vacuum pump is installed at the site of greatest heating of the mass. If we place an optional chamber whose diameter is the same as that of the worm at the site of the molding head of the extruding press, extrusion of the mass will not then take place, but a typical worm compression molding. In this manner the freshly prepared propellant mass can be extruded either directly into the engine chamber or into a form, in which it undergoes its final hardening.

Single-worm extruding presses have one disadvantage in that sometimes the extruded mass sticks to the worm and revolves with it, so that so-called clogging of

the extruding press occurs. Multi-worm extruding presses do not have this disadvantage; they produce a uniform output and permit the attainment of a very high pressure in the head. The overlapping convolutions prevent adhesion of the particles of the material and their rotation with the worms. Due to the contiguity of the convolutions, there is practically no backflow of the treated mass.

Although there are many examples for the mathematical conception of the functioning of a worm extruding press, previous construction designs have primarily been based on intuition and the experience of the builder. The mathematical conception of this problem is difficult due to the presence of many superimposed variables. For a mathematical conception, it would be necessary to determine not only the dimensions of the worm (length, diameter, the angle of inclination of the helices, the depth and width of the flow grooves, etc.), the molding head, the cylinder, the number of revolutions of the worm, the capacity, the heat balance and the pressure at the delivery end of the extruding press; but also the interactions at the individual points of the cylinder surface between the surface of the worm and the advancing mass. Finally, it would also be necessary to know the characteristics of the mass which the extruding press is designed to process. It is particularly necessary to know the dependence of the viscosity of this mass on the temperature, flow rate and kneading time. Previous tests of the analytical concept for all processes taking place in single- and multi-worm extruding presses were carried out with a number of simplified assumptions and for comparatively simple systems [118,119], but the practical usefulness of the resultant equations is not satisfactory for the designer nor for the user. Nevertheless, a knowledge of these equations together with the many experimentally obtained functional relations between the individual parameters [18] permits the designer to determine some structural data separately, and the consumer to select appropriate work parameters or to choose the type of extruding press best suited for handling masses with precisely specified properties.

All these mathematical concepts can be found in domestic [119] and foreign [118] literature.

From the point of view of solid rocket propellant technology, it is of primary importance to determine the properties of the mass which is to be extruded in order to be able to choose an appropriate worm extruding press from the existing types or to provide the designer with the necessary requirements. Accordingly, it is necessary to ascertain the following characteristics of the mass to be extruded:

- (1) the maximum extrusion temperature (for reasons of safety),
- (2) the dependence of the viscosity of the mass on the temperature,
- (3) the dependence of viscosity variations (for composite fuels) on the percent of crystalline filler content (equation 3.8),
- (4) the dependence of the viscosity on the feed rate for individual temperatures,
- (5) the dependence of the viscosity on the kneading time,
- (6) the content of volatile substances at the permissible extrusion molding temperature,
- (7) adherence to the metal as a function of the temperature.

All these data can be determined under laboratory conditions. It is necessary to determine the permissible extrusion temperature by heating the mass and observing its susceptibility to friction determined as a function of the temperature will be much more conclusive in the determination of the permissible extrusion temperature.

Points 2 to 5 can be determined most accurately with a Hoppler consistometer, with which it is possible to determine the viscosity from several hundred to above  $10^9$  cp.

The volatile substances in the extruded mass can be the solvent, monomer residues of the substance used, reaction products evolving during the extrusion ( $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ) and traces of air. There are many methods of degassing the extruded mass and all of them furnish good results [118], although the problem itself was initially very complex. At the present time, all solutions are based approximately on the following operations which take place in the extruding press: plasticization of the mass, compression (by employing a slower feed rate), expansion (faster feed),



drawing off of the gases (the previously compressed gas bubbles disrupt the mass upon expansion and the gas escapes to the draw-off, which can additionally be connected to a vacuum pump), renewed compression and extrusion.

A very important factor is the adherence of the mass to the metal which comprises the worm and the cylinder, i.e., the so-called coefficient of friction. This coefficient reaches a maximum at a definite temperature for most masses. When passing to lower temperatures the mass takes on the nature of a solid and has a lower coefficient of adherence; on the other hand, at higher temperatures it assumes the properties of a liquid and slides over the metal surface. Therefore, it is of prime importance in this case to determine the temperature at which the coefficient of friction attains its maximum value. When the coefficient of friction is known for the individual temperatures, it is possible to determine the optimal angle of inclination of the helices of the worm in the individual zones of the extruding press. All these data on the extruded mass and the desired extrusion pressure resulting from them facilitate the determination of all the requirements imposed on the extruding press.

On the basis of a number of interdependence curves for the individual parameters, given in [118], we can determine the size of the worm, the depth of its channel, the heating and cooling systems, the r.p.m., the power required to turn the worm, the angle of inclination of the helices, the type of degassing system, etc. However, it must be borne in mind that the propellant masses obtained, particularly the composite fuels, generally have a rather high coefficient of viscosity. For example, when the combustible component-binder mixture used is in a syrupy state, the introduction of about 80% inorganic crystalline oxidizing substance will increase its viscosity by as much as several hundred times. In individual cases this viscosity may reach a value of the order of  $10^{10}$  cp. The power rating of the extruding press must be very great with such high viscosities and when profiles with large diameters are shaped. A high viscosity also requires the use of small passages (furrows) of the worm, and this in turn leads to a reduction in the capacity of the

extruding press. Accordingly, decreasing the viscosity of the mass to be extruded is a very important problem in propellant charge technology.

After appropriate selection of the components, it is possible in the case of composite fuels to reduce the viscosity by employing somewhat higher extrusion temperatures than with colloidal fuels, because the former usually have a higher temperature of excitation (detonation).

In some masses extruded with worm extruding presses, a structural spatial orientation of the finished propellant is detected [7]; this affects its burning rate; for example, some propellants have a 15% higher burning rate in the direction of extrusion than in a perpendicular direction.

### 3.3.3. Casting

The most suitable method of propellant charge preparation is casting. This method lends itself to both composite and colloidal fuels (with correctly chosen amounts of plasticizer and low-melting components). In the case of composite fuels, the combustible component raw material is usually a monomer (a liquid) with an oxidizer (a solid powdered crystalline mass), which after mixing is poured into forms, where polymerization takes place. The charge thus assumes the shape of the casting form. We encounter the following problems with this type of technology: suspension formation, sedimentation, degassing of the suspensions, etc. In the following, the monomer with its additives, such as plasticizers, catalyzers, activators, polymerization regulators, etc., is called the liquid, and the oxidizing substance with all its crystalline additives, the solid.

The solid added to the liquid is heterogeneous with respect to crystal size and also frequently with respect to the density (since it is a mixture of various oxidizers and other inorganic additives); therefore, from the time the crystals are mixed with the liquid until polymerization, the suspended crystal of the solid substance tends to sink. The following undesirable effects can take place during the precipitation:

(1) separation of the coarse crystals on the bottom from the fine crystals in the upper portion of the form due to the difference in the precipitation rate,

(2) separation of the denser substances from the less dense substances due to a possible difference in the densities of the solids,

(3) in the deposit formation process, a greater concentration of the material being deposited occurs on the bottom of the form and a lesser concentration in the upper portion of the form.

These undesirable effects can be partially or completely avoided through a knowledge of the laws that govern them.

The settling effect of solids in a liquid can be of 2 types. In the first case, when the settling solids do not interact with each other, i.e., the solid phase concentration is low, we can consider the settling of the individual crystals to be caused solely by the force of gravity. In the second case, when the phase concentration is so great that the movement of the liquid around one crystal affects the settling of another crystal, there is a settling of the entire suspension as a level; and above this, a clear liquid. This type of settling is called sedimentation. It is possible to encounter both types of settling in solid rocket propellant technology; therefore, it is necessary to give careful consideration to both the free settling of solids in a liquid and sedimentation.

The settling of the crystals of a solid in a liquid under the influence of gravity depends on the viscosity of the liquid, the size and shape of the crystals, the density of the solid, the interfacial tension between the solid and the liquid, etc. For the sake of simplification we consider the settling of spherical solids. The rate of settling is uniformly delayed in the initial period; then after a certain period of time, when the force of gravity on the crystal becomes equal to the resistance of the medium, it begins to settle with a constant velocity. For all practical purposes, this uniform motion is reached very quickly and is therefore essential in the settling effect.

If a certain spherical body with diameter  $d$  and density  $\gamma_s$  settles in a liquid

of density  $\gamma$ , the force of gravity  $\underline{W}$  will be

$$W = \frac{\pi d^3}{6} (\gamma_s - \gamma) \quad (3.11)$$

The resistance of the liquid in the case of a free fall of the sphere can be represented by the equation

$$R = \lambda \frac{\pi d^2}{4} \frac{U^2}{2g} \gamma \quad (3.12)$$

where:  $\lambda$  = the coefficient of resistance,

$\pi d^2/4$  = the area of the profile of the body,

$U$  = the rate of fall (settling).

In the stabilized settling the force of gravity is equal to the resistance,  $W = R$ ; thus, we have the relationship

$$\lambda = \frac{4}{3} \frac{d (\gamma_s - \gamma) g}{U^2 \gamma} \quad (3.13)$$

Because  $\lambda$  is a function of  $Re$  (the Reynolds number), both the velocity  $\underline{U}$  and the diameter  $\underline{d}$  appear on both sides of the equation. This equation is not suitable for calculating the settling rate of the given particles or for calculating the diameter of particles settling at a given rate. It is well known that other mathematical dependences of  $\lambda$  on  $Re$  are valid for different ranges of the Reynolds number. The ranges of the  $Re$  number and a description of the phenomena in these ranges are presented in Table 3.3.

In calculating the settling rate, it is best to multiply both sides of the equation (3.13) by  $Re^2$  (the right side by the derived  $Re$  value); we then obtain

$$\lambda Re^2 = \frac{4 d^3 (\gamma_s - \gamma) g}{3 \mu^2 g} \quad (3.14)$$

By calculating the right side of the equation, we obtain the value of the product  $\lambda \cdot Re^2$ . Using the value for  $\lambda$  as a function of  $Re$  (Table 3.4), we can calculate

TABLE 3.3. A PRESENTATION OF THE LAWS GOVERNING THE SETTLING OF SOLIDS IN LIQUIDS

No.	Range of Re number	Dependence of $\lambda$ on Re for spheres	Law which applies	Description of effect	Dependence of $\lambda$ on Re for nonspherical bodies
1	$Re < 10^{-4}$	-	-	Comminution is so small that settling is disturbed by the Brownian movement.	-
2	$10^{-4} < Re < 2$	$\lambda = \frac{24}{Re}$	Stokes' law	Flow of liquid around spheres has a laminar nature. The viscosity plays an important role.	$\lambda = \frac{24}{Re^{0.843}} \cdot \frac{1}{\log \frac{\Psi}{0.065}}$
3	$2 < Re < 500$	$\lambda = \frac{18.5}{Re^{0.6}}$	Allen's law	Resistance depends to a lesser degree on the viscosity. Transitory motion from laminar to turbulent	*
4	$500 < Re < 2 \cdot 10^5$	$\lambda = 0.44$	Newton's law	The flow of the liquid around the spheres has a turbulent nature.	$\lambda = 5.31 - 4.88\Psi$

\*For the dependence of  $\lambda$  on  $\Psi$ , see Kalendarz Chemiczny, Vol. II(1), p. 721. PWT, Warsaw 1955.

the value of  $\lambda \cdot Re^2$  as a function of Re.

When the specific value of this product is known, we find the corresponding Reynolds number; hence the settling rate of sphere is determined when its diameter is known.

The most convenient method of determining the diameter of a sphere with a known settling rate is dividing equation (3.13) by Re (the right side of the equation by the derived value of Re)

$$\frac{\lambda}{Re} = \frac{4}{3} \cdot \frac{K^2 \mu (\gamma_0 - \gamma)}{\gamma^2 U^3} \quad (3.15)$$

The values of the Reynolds number and the dependencies of the coefficient of resistance on the Reynolds number given for these values are approximate at the extremes of the individual ranges. In some publications these values may be somewhat different; nevertheless, bearing in mind the decreased accuracy of the calculations, the cited dependencies for  $\lambda$  can be used even as the extreme of a given range is approached. The extremes of the ranges also vary with varying sphericity of the crystals; therefore, the equations given in the last section for particles of low sphericity are not valid for extreme values of the Re number ranges.

After calculating the right side of equation (3.15), we have the value of the quotient  $\lambda/Re$ . From Table 3.4 it is possible to calculate the dependence of the value of this quotient on the Re value, from which the diameter of the particle is calculated when the settling rate is known. For this purpose it is most convenient to set up a similar table of the dependency of the  $\lambda/Re$  quotient on the Reynolds number.

TABLE 3.4. COEFFICIENT OF RESISTANCE FOR DIFFERENT Re VALUES DURING MOVEMENT OF SPHERES IN A LIQUID

Re	$\lambda$	Re	$\lambda$	Re	$\lambda$	Re	$\lambda$
0.1	240	10	4.1	700	0.50	$5 \cdot 10^4$	0.49
0.3	80	20	2.55	1,000	0.46	$7 \cdot 10^4$	0.50
0.5	49.5	30	2.00	2,000	0.42	$1 \cdot 10^5$	0.48
0.7	36.5	50	1.50	3,000	0.40	$2 \cdot 10^5$	0.42
1.0	26.5	70	1.27	5,000	0.385	$3 \cdot 10^5$	0.20
2.0	14.4	100	1.07	7,000	0.39	$4 \cdot 10^5$	0.084
3.0	10.4	200	0.77	10,000	0.405	$6 \cdot 10^5$	0.10
5.0	6.9	300	0.65	20,000	0.45	$1 \cdot 10^6$	0.13
7.0	5.4	500	0.55	30,000	0.47	$3 \cdot 10^6$	0.20

In the case of nonspherical particles, the concept of sphericity  $\Psi$  and the concept of the substitutional diameter  $d_z$  are also introduced.

The sphericity  $\Psi$  is the ratio of the surface area of a sphere with the same volume as the particle to the surface area of the particle. The sphericity of a crystal is readily calculated by assuming that it can be broken down into crystals similar to it due to the regularity of the crystalline lattice.

The substitutional diameter  $d_z$  is the diameter of a ball having a volume equal to the volume of the nonspherical particle. The coefficient of resistance in the case of nonspherical particles depends not only on the Re number but also on the sphericity  $\Psi$ , which are given in Table 3.3 for individual ranges.

Introduction of the substitutional diameter  $d_z$  and sphericity  $\Psi$  can be carried out only for isometric particles, i.e., those which have all 3 axes commensurate; this method can not be used for long needles and thin flakes.

However, it is possible to encounter non-isometric particles in solid rocket propellant technology, e.g., the metallic aluminum and magnesium frequently used in composite fuels occur in the form of thin flakes.

Oriental calculations have already indicated that in the case of comminutions of oxidizing substances (to 200 microns) used in composite solid propellant technology, with rather high viscosities of the liquid (100 cp and up) and with rather high densities of the crystalline components (from 1 to 3 g/cm<sup>3</sup>)\*, the settling takes place primarily in a laminar manner. From these data we can determine approximately which law applies to the settling taking place. In this case, when we know that we can apply a particular law to a given suspension, calculation of the particle diameter given the velocity, or the settling rate given the diameter, is simplified. Then we introduce the  $\lambda$  values from Table 3.4 in equations (3.14) and (3.15); and inserting the developed form of Re, we calculate  $U$  or  $d$ . Thus, it is possible to formulate an equation in  $U$  and  $d$  for each range of the Re number. If

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\*Translator's note: Given in original as g/cm<sup>2</sup>



$Re < 10^{-4}$ , for all practical purposes the solid is suspended in the liquid and the particles covered by this range are carried away by larger particles which settle in accordance with the Stokes, Allen or Newton laws.

For spheres conforming to Stokes' law, we obtain the settling rate

$$U = \frac{d^2 (\gamma_s - \gamma)}{18 \mu} \quad (3.16)$$

Hence we can easily find the maximum sphere diameter for which this equation can be used. It is evident from Table 3.3 that  $Re < 2$  is the condition of Stokes' law applicability. After substituting the derived form of  $Re$  in this inequality and then substituting the expression (3.16) in place of  $U$ , we obtain

$$d < \sqrt[3]{\frac{36 \mu^2 g}{\gamma (\gamma_s - \gamma)}} \quad (3.17)$$

Then if the specific weight and viscosity of the liquid and the density of the sphere are known, we can calculate the right side of the latter inequality. If the given diameter is less than this value, Stokes' law can then be applied to the settling of the ball.

In an analogous manner, the settling rate within the range of applicability of Stokes' law and the maximum substitutional diameter can be derived for isometric nonspherical particles

$$U = \frac{K_s d_s (\gamma_s - \gamma)}{18 \mu} \quad (3.18)$$

$$d_s < \sqrt[3]{0.9 \frac{\mu^2 g}{K_s \gamma (\gamma_s - \gamma)}} \quad (3.19)$$

where  $K_s = 0.843 \log(\psi/0.065)$ .

In order to find the equation in  $d_s$ , the condition  $Re < 0.05$  is necessary because the range of Stokes' law applicability for nonspherical particles varies with varying sphericity, and the law is valid for all configurations only under this

condition.

The settling rate and the allowed ball diameter limits are determined in like manner in the case of Allen's law application.

$$U = \frac{0.153 d^{1.15} (\gamma_s - \gamma)^{0.71}}{(\gamma/\mu)^{0.29} \mu^{0.43}} \quad (3.20)$$

$$1.93 \sqrt[3]{\frac{\mu^2 g}{\gamma (\gamma_s - \gamma)}} < d < 59 \sqrt[3]{\frac{\mu^2 g}{\gamma (\gamma_s - \gamma)}} \quad (3.21)$$

Allen's law is not valid for nonspherical particles (the dependence of  $\lambda$  on  $Re$  and  $\psi$  has no mathematical formulation). Therefore, in the range  $2 < Re < 500$ , the settling rate is calculated by the trial and error method from equation (3.13). The settling rate of a particle with a given sphericity is established and  $Re$  is calculated on this basis. We learn the value of the coefficient of resistance  $\lambda$  from the  $Re$  and  $\psi$  values (see reference in Table 3.3) and we calculate  $U$  from equation (3.13). If the calculated value does not agree with the assumed one, another approximation is performed in the same way.

As already mentioned, we are discussing the laminar motion of a solid in a liquid with respect to solid rocket propellant technology; in this connection, a consideration of the settling in accordance with Newton's law can be dispensed with. Let us consider the following example.

In order to determine the settling laws of ammonium perchlorate in an unhardened resin, the free settling of a single crystal having a mass of 0.0010 g was studied experimentally. The density of  $NH_4ClO_4$  is  $1.95 \text{ g/cm}^3$  and the settling rate, 0.005 m/sec (assumed). An attempt was made to determine the sphericity of an  $NH_4ClO_4$  crystal (assuming that the grains have a similar configuration due to crystalline structure and the grinding method) and to determine the settling rate for several smaller grain sizes used in practice. (The calculated values given may not be used for specific configurations, but are only indicative of the calculation method.) Having the weight of the studied grain (0.001 g) and the density

(1.95 g/cm<sup>3</sup>), we calculate its volume

$$V = \frac{m}{\rho} = \frac{0.001}{1.95} = 0.00055 \text{ cm}^3$$

This permits the determination of the substitutional diameter  $d_z$  of this grain, or the diameter of a ball having the same volume:

$$d_z = \sqrt[3]{\frac{6 \cdot V}{\pi}} = \sqrt[3]{\frac{6 \cdot 0.00055}{3.14}} = 0.101 \text{ cm} = 1 \cdot 10^{-3} \text{ m}$$

If we have the settling rate of these grains  $U = 0.005 \text{ m/sec}$ , the density of the unhardened resin  $1000 \text{ kg/m}^3$ , its viscosity  $\mu = 100 \text{ cp}$ , then  $\mu g = 0.10 \text{ kg/m} \cdot \text{sec}$  (the viscosity is expressed in units of  $1 \text{ cp} = [10^{-3}/9.81] \text{ kg} \cdot \text{sec/m}^2$ ). Hence, we determine the Reynolds number for this settling with the following equation:

$$Re = \frac{U d \gamma}{\mu g} = \frac{5 \cdot 10^{-3} \cdot 10^{-3} \cdot 10^3}{0.1}$$

$$Re = 5.0 \cdot 10^{-2}$$

With such a small Reynolds number the settling proceeds in accordance with Stokes' law, and the coefficient of resistance is

$$\lambda = \frac{24}{Re \cdot 0.843 \lg \frac{\psi}{0.065}}$$

We calculate the sphericity of the particles from the equation for the settling rate under Stokes' law:

$$U = \frac{K_s \cdot d_z^2 (\gamma_s - \gamma)}{18 \mu}$$

$$K_s = \frac{18 U \mu}{d_z^2 (\gamma_s - \gamma)} = \frac{18 \cdot 5 \cdot 10^{-3} \cdot 10^{-1}}{10^{-6} \cdot 950 \cdot 9.81} = \frac{9 \cdot 10^{-3}}{9.32 \cdot 10^{-3}}$$

$$K_s = 0.9656$$

$$K_1 = 0.843 \lg (\psi/0.065) = 0.9656$$

$$\lg (\psi/0.065) = 1.1455$$

$$(\psi/0.065) = 13.98$$

$$\psi = 0.9087 \approx 0.9$$

We can determine the coefficients of resistance for the entire Reynolds number range with the aid of the sphericity.

In the case of Stokes' law we make use of the dependence

$$\lambda = \frac{24}{0.843 \lg (\psi/0.065) \text{Re}} - \frac{25}{\text{Re}}$$

If we wish to calculate the diameter for individual Reynolds numbers in the range of Stokes' law, it is more convenient to calculate the product directly using

$$\lambda \text{Re}^2 = 25 \text{Re}$$

The values of this quantity are given in the following Table

Re	$4 \cdot 10^{-3}$	$10^{-3}$	$8 \cdot 10^{-4}$	$2 \cdot 10^{-4}$	$10^{-4}$
$\lambda \text{Re}^2$	0.1	0.025	0.02	0.005	0.0025
d [mm]	0.43	0.278	0.251	0.16	0.127
U [mm/sec]	0.93	0.36	0.318	0.125	0.08

From the equation

$$\lambda \text{Re}^2 = \frac{4}{3} \frac{d^3 (\gamma_s - \gamma) \gamma}{\mu^2 g}$$

we calculate  $\underline{d}$  as a function of  $\lambda \text{Re}^2$

$$d = \sqrt[3]{\frac{3 \mu^2 g}{4 (\gamma_s - \gamma) \gamma} \lambda \text{Re}^2}$$

$$d = \sqrt[3]{\frac{3 \cdot 10^{-2}}{4 \cdot 9.81 \cdot 950 \cdot 10^3} \lambda \text{Re}^2}$$

$$d = \sqrt[3]{8.05 \cdot 10^{-10} \lambda \text{Re}^2}.$$

Using the above equation, we calculate the diameters for the individual values of the product  $\lambda \cdot \text{Re}^2$ , which is given in the Table. It follows from these values that under the conditions of the perchlorate comminution used, the settling takes place either within the scope of Stokes' law; or, in the case of finer crystals, the crystals for all practical purposes are suspended in the resin.

When the  $\text{Re}$  and  $d$  values are known, we can calculate the settling rate of the individual grains on the basis of the Reynolds number definition

$$U = \frac{\text{Re} \mu g}{d \gamma} = \frac{\text{Re}}{d} 10^{-4}$$

The results of the calculations for several grain sizes are given in the Table. The sizes calculated for one crystal type can serve to determine the sizes of the crystals of another substance, in order to achieve an identical settling rate.

It is evident from this example that in the case of the usual oxidizing substance comminutions, the usual viscosity of the unhardened resins and densities of the substances, the settling proceeds either in a laminar manner (Stokes' law) or the solid substance is for all practical purposes suspended in the liquid. Thus, it follows that there is no great danger of a separation of the small oxidizing substance crystals from the large ones because, as the large crystals settle, they will carry along the small ones, which would not settle by themselves.

From this example we also have a means of preventing the separation of crystals with different densities, namely: by achieving a finer comminution of substances with greater densities and a coarser comminution of substances with lower densities, we can obtain an identical settling rate.

As already mentioned, we have hitherto considered the free settling of solids in a liquid, i.e., a settling such that the motion of one crystal does not interfere with the settling of another.

In the actual preparation of solid propellants, we are frequently dealing with the inclusion of a maximum amount of oxidizing substance (up to 80%) in relation to the binder. In these cases we have nonfree settling. Settling then essentially takes place in the entire mass: a so-called sedimentation takes place, i.e., the settling of a deposit as a layer, above which a layer of clear liquid forms. If the suspension is sufficiently dilute, a dense phase, a loose phase and, in the upper portion, a clear liquid phase are formed immediately after mixing. Toward the end of sedimentation the loose phase gradually assumes the concentration of the dense phase, and its size gradually decreases in favor of the dense and pure liquid phases. In time the dense phase "swallows up" the entire loose phase and only the liquid and dense phases of the suspension remain. From the time of formation, the dense phase continually increases in concentration; and its surface, after the disappearance of the thin phase, settles with a uniform motion until it reaches a maximum concentration. In the case of very concentrated suspensions there is only the dense phase from the beginning to the end of sedimentation, and its surface settles slowly.

This settling rate can be represented as follows:

$$U = U_s f(\epsilon)$$

where:  $U_s$  = the rate of free settling of a single deposit grain in accordance with Stokes' law,

$f(\epsilon)$  = empirical function of the porosity of the deposit (the porosity is that fraction of volume of the free space between the grains of the deposit).

For loosely packed deposits

$$f(\epsilon) = \epsilon^2 \cdot 10^{-1.82(1-\epsilon)}$$

where:  $\epsilon = V_c / V_c + V_s$ ;  $V_c$  and  $V_s$  = the volume of the liquid and the volume of the solid, respectively.

For tightly packed deposits, i.e., when  $\epsilon \leq 0.7$ , this function can be represented by the simpler equation

$$f(\epsilon) = 0.123 \frac{\epsilon^3}{1 - \epsilon}.$$

In solid propellant technology, the second equation is more applicable because here we have more concentrated suspensions.

As we know from the preceding considerations

$$U_s = \frac{1}{18} \frac{d^2 (\gamma_s - \gamma)}{\mu}$$

in the case of true spheres, while in the case of spherical particles

$$U_s = \frac{K_s d^2 (\gamma_s - \gamma)}{18 \mu}.$$

Thus, the rate of sedimentation for spheres and for spherical lumps can be determined from the following equations:

$$U = \frac{d^2 (\gamma_s - \gamma)}{18 \mu} 0.123 \frac{\epsilon^3}{1 - \epsilon}$$

$$U = \frac{K_s d^2 (\gamma_s - \gamma)}{18 \mu} 0.123 \frac{\epsilon^3}{1 - \epsilon}$$

If we assume the rate of free fall to be known, then the sedimentation rate will be a function only of the porosity  $\epsilon$ . At the beginning of sedimentation, the porosity of the deposit can be calculated easily; but as time goes on the porosity of the deposit decreases and can be expressed as a function of the level of the deposit in the form of a simple expression. The dependence of the rate on the height derived in this manner can be used to calculate the settling time up to the moment when the settling is complete, or the height of the column of completely settled deposit. Numerous examples of these calculations can be found in the domestic literature [35].



A knowledge of the time required for a complete settling of the deposit is necessary in order to be able to establish the time after which the binder, being hitherto in a liquid state, can be permitted to harden (amount of catalyst). The deposit obtained during the sedimentation process is usually thickest on the bottom of the vessel and thinnest in the upper portion. However, this density distribution is not directly proportional to the height. In most cases, the density of a completely settled deposit varies but little from the bottom to the top of the column. There is a distinct decrease in the solid phase concentration only at a certain level, at the upper surface. Therefore, it frequently occurs in the practical preparation of solid propellant charges that the upper portion of the charge is pared off as being distinctly different in density than the remainder. In this way sufficiently homogeneous charges are obtained (density differences sometimes cannot be detected).

An important problem in the technology of obtaining cast charges is the elimination of gas (air) bubbles from the cast mass. The disadvantage of air bubbles lies in a reduction of the mechanical strength of the charge, an undesirable, frequently irregular increase in the burning rate and a decrease in the charging density of the engine. We can avoid air in the cast charges by skillful preparation of the solid-liquid suspension, by an equally careful mixing of the suspension, by employing a vacuum during casting, etc.

In preparing a mixture of a solid with a liquid it is necessary to wet the solid thoroughly with the liquid before immersion so that the number of entrained bubbles is reduced. Subsequently, by slow (not "turbulent") mixing, the few suspended bubbles are removed to such an extent that the cast charge is good enough without vacuum degassing.

Vacuum degassing is not convenient because it increases the cost of charge production and is not suitable for compositions which contain both low boiling and high boiling liquid substances. In this case the binder composition would change during the degassing process.

Vacuum degassing is difficult when it is necessary to degas a thick layer of

suspension. Therefore, it is frequently useful to employ vacuum degassing in the preparation of the mass to be cast; then the degassing takes place directly in the entering stream and in the successive thin layers cast.

As we can see, a whole series of quite divergent problems, which must be worked out in a distinct mutual arrangement, is involved in solid propellant technology. There is still no thorough knowledge of technology in this field and the above remarks are only generally indicative of the problems which may be encountered.

All the data in the literature indicate that the most widely used technological method in solid propellant production is casting. Consequently, this method receives the broadest treatment in this work.

With respect to other problems involved in this method, we must also mention the problem of oxidizer comminution. This comminution must be precisely defined in order to achieve a definite burning rate and appropriate fluidity of the mass. Fluidity of the mass before hardening can be achieved not only by employing a combustible component -- binder with a low viscosity but also by applying a proper determination of solid particle dimensions. Certain complexes of particle dimensions are used instead of crystals of one size. This facilitates filling all the gaps between the large crystals with small crystals. Sometimes, the so-called castability of the mass is improved by the use of appropriate plasticizers or surface-active substances. The oxidizer, when mixed with the binder (a liquid combustible substance), is ready for casting into appropriate forms, where a hardening of the mass takes place. Hardening can be carried out at ambient or raised temperatures and depends on polymerization or vulcanization of the binder -- combustible substance. A suitable core is placed in the charge before hardening if the charge is to have an internal channel. This core is removed after the charge has hardened; in order to facilitate removal, it is coated with an appropriate layer of a substance (teflon, wax, etc.) or the core is given the proper taper.

At the present time, the production of composite solid propellants is exclusively periodic. Therefore, the ballistic characteristics of these propellants are

to a certain extent variable, depending on the batch. This disadvantage could be eliminated only by introducing continuous production [7].

#### 4. INTERPHASE (SURFACE) PHENOMENA

Recently, a great deal of importance has been placed on the question of surface-active agents for use in rocket fuel production.

These agents not only increase the possibility of "cramming" larger amounts of dispersed substances (particularly the oxidizer) in the same amount of combustible component, but also increase the stability of the resultant dispersion as well as the stability of the fuel by separating the monomolecular oxidizer layer from the combustible component.

Surface-active agents are substances which lower the surface tension on the boundary of two phases.

Most surface-active agents have a linear molecular structure whose length considerably exceeds the cross section. The molecules of these substances have 2 elements -- a philic group and a phobic group -- and they always arrange themselves perpendicular to the surface of the separated phase. Molecules of this type may also contain additional groups, but all these groups must be located along one side in order to preserve the polarity of the molecules. For example, the hydrophilic groups are:  $-\text{COOMe}$ ,  $-\text{SO}_3\text{Me}$ ,  $-\text{O}-\text{SO}_3\text{Me}$ , the hydrophobic groups are hydrocarbon chains, preferably with 12 to 18 carbon atoms in a simple chain.

Surface-active substances which dissociate electrolytically are called ionogenic or ionic, while nondissociating ones are called nonionic. The former group includes organic substances, e.g., of the  $-\text{COOMe}$  group; the latter, of the  $-\text{OH}$  group.

Ionogenic substances are divided as follows according to activity:

- (a) anionic,
- (b) cationic.

If the phobic chain contains an anion, it is an anionic surface-active substance, e.g.,  $\text{C}_{17}\text{H}_{35}\text{COO}^-$

An active substance containing a phobic cation in the chain, e.g.,  $\text{RNH}_3^+$ , will

be cationic.

Ampholytic substances are also known. They have 2 philic groups, one anionogenic and another cationogenic, e.g., cetylaminooacetic acid  $C_{16}H_{33}NH_2CH_2COOH \rightleftharpoons C_{16}H_{33}NH_2^+CH_2COO^-$ .

#### 4.1. Surface and Interphase Tension

On the boundary of 2 phases there is a surface layer of very small thickness, but differing in properties from the 2 phases in question. This layer is the result of the inequality of the Van der Waals forces acting on the molecules located on the surface or just under the surface, whereas these forces acting on the molecules inside the substance become equalized.

Because the action of the Van der Waals forces is inversely proportional to the seventh power of the distance between the molecules, the range of these forces for all practical purposes does not exceed twice the diameter of the molecules. Consequently, the surface layer consists of 2 monomolecular layers at the most.

Because of the large distances between the molecules in a gas, the effects of the Van der Waals forces are negligible. These forces between the gas and liquid molecules in the surface layer are also small and can be disregarded.

The forces acting on the surface layer molecules endeavor to draw these molecules into the liquid. Thus, the surface layer exerts a certain amount of pressure on the liquid. In small amounts of a liquid, when the force of gravity is comparable to the surface forces, it can be observed that every liquid will endeavor to fill the smallest volume by assuming a spherical form.

Thus, the surface layer has a certain energy reserve. The work required to increase the surface area by one unit (e.g.,  $1 \text{ cm}^2$ ) is the so-called surface energy  $\sigma$ . The total energy contained in a given surface is called the free surface energy

$$\sigma = \left( \frac{\partial f}{\partial a} \right)_{T, P}$$

where:  $\partial f$  = the free energy increment,

$\Delta q$  = the increase in surface area.

The surface energy frequently replaces the hypothetical concept of surface tension. It is defined as the force acting tangent to the surface on a section of unit length. The force has a vector perpendicular to this section. Evidently, forces that are tangent to the surface do not act on it. This is simply a mathematical concept arising from the fact that the surface tension, expressed in dyne/cm, and the surface energy, expressed in erg/cm<sup>2</sup>, have the same magnitude m·t<sup>-2</sup>.

$$\frac{\text{dyne}}{\text{cm}} = \frac{\text{g}}{\text{sec}^2} [\text{m} \cdot \text{t}^{-2}] \quad \frac{\text{erg}}{\text{cm}^2} = \frac{\text{g}}{\text{sec}^2} [\text{m} \cdot \text{t}^{-2}]$$

The surface tensions of most liquids (Table 4.1) rarely exceed 50 dyne/cm. The surface tension decreases with increasing temperature, and  $\sigma = 0$  at the critical temperature.

TABLE 4.1. THE SURFACE TENSIONS OF VARIOUS LIQUIDS AT 20°C

Compound	$\sigma$ [dyne/cm]	Compound	$\sigma$ [dyne/cm]
Acetone	23.70	Nitrobenzene	43.9
Benzene	28.88	Nitroethane	32.2
Chloroform	27.1	Nitromethane	36.82
Ethyl ether	17.01	Styrene	32.14
Glycerine	63.4	Toluene	28.5
Ethylene glycol	47.7	Water	72.8

#### Interfacial tension

If the attractive (adhesive) forces between the molecules of two different substances are greater than the cohesive forces between the molecules of the individual substances, these substances then mix together, forming solutions, and there are no separate phases. On the other hand, if the attractive forces between the molecules of each substance by itself are greater than the attractive forces between the

molecules of these 2 substances, an interface then results, and also an interfacial tension  $\sigma_{1,2}$  (between phases 1 and 2).

The interfacial tension is always less than the surface tension of the substance having the greater tension by the value of the attractive force between the 2 substances. The Antonoff rule is most frequently satisfied for liquids

$$\sigma_{1,2} = \sigma_1 - \sigma_2$$

if these liquids are mutually saturated.

Work is required to separate the 2 liquids. The work required on  $1 \text{ cm}^2$  of surface is called the work of adhesion. It is defined by the Dupre equation

$$A_{ad} = \sigma_1 + \sigma_2 - \sigma_{1,2} \quad (4.1)$$

If  $\sigma_{1,2} = 0$ , then for a homogeneous liquid

$$\sigma_1 = \sigma_2 \text{ and } A_{coh} = 2\sigma_1$$

This is the so-called work of cohesion, or the cohesion of the liquid.

Solids also have surface tension but, because of the immobility of the molecules in the crystalline lattice, the work required to increase the surface area cannot be measured directly. Thus, indirect methods are used; however, these are not very accurate.

TABLE 4.2. INTERFACIAL TENSION BETWEEN WATER AND ORGANIC LIQUIDS AS WELL AS SOLID SUBSTANCES

Substance	$\sigma_{1,2}$ [dyne/cm]	Substance	$\sigma_{1,2}$ [dyne/cm]
Benzene	35	PbO <sub>2</sub>	1,800
Chloroform	32.8	CaF <sub>2</sub>	2,500
Ethyl ether	10.7	CaSO <sub>4</sub> ·2H <sub>2</sub> O	1,050
Nitrobenzene	25.66	PbF <sub>2</sub>	900
Styrene	35.48	PbI <sub>2</sub>	130



TABLE 4.2. SURFACE TENSIONS OF INORGANIC COMPOUNDS ABOVE FUSION TEMPERATURE

Compound	t. [°C]	$\sigma$ [dyne/cm]	Compound	t. [°C]	$\sigma$ [dyne/cm]
$K_2Cr_2O_7$	420	170.1	$NaNO_3$	322	119.7
$KNO_3$	380	110.4	$LiNO_3$	359	111.5

Interfacial tension is also present between a solid and a liquid. Experiments have shown that the surface tensions of solids are much greater than those of liquids (Table 4.2).

### Three interfaces

The action of surface-active agents often takes place at a three-phase interface: a solid -- a liquid -- a gas, a solid -- a liquid -- a liquid, a gas -- a liquid -- a liquid.

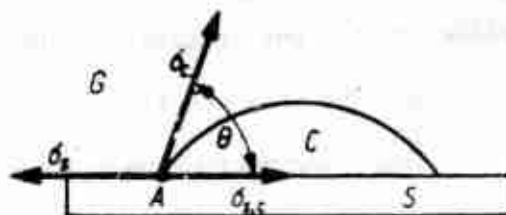


Figure 4.1. Equilibrium of the 3 phases:  
G = gaseous, C = liquid, S = solid.

A solid, a drop of liquid and a gas are shown in equilibrium in Figure 4.1. All 3 phases meet at point A. Because equilibrium is maintained, it follows that the resultant of forces  $\sigma_c$ ,  $\sigma_s$  and  $\sigma_{s,c}$  must be equal to zero,

$$\sigma_s = \sigma_{sc} + \sigma_c \cos \theta$$

The work of adhesion of the liquid-solid, in accordance with equation (4.1), is

$$A_{ad} = \sigma_c + \sigma_s - \sigma_{sc}$$

$$A_{ad} = \sigma_c (1 + \cos \theta)$$

In measuring angle  $\theta$ , it is not necessary to know  $\sigma_s$  (or the surface tension of the solid, which does not lend itself to measurement) in order to determine the work of adhesion; angle  $\theta$  is called the boundary angle.

If angle  $\theta = 0$ , then  $A_{ad} \geq 2\sigma_c$  and wetting is complete, the solid attracts the liquid with a force which is at least equal to the attractive force between the molecules of the liquid itself; the liquid forms a thin film on the surface of the solid.

If  $0^\circ < \text{angle } \theta < 90^\circ$ , then wetting is good; whereas if  $90^\circ < \text{angle } \theta < 180^\circ$ , wetting is poor. On the other hand, it does not happen that angle  $\theta = 180^\circ$ .

If  $A_{ad} > 2\sigma_l$ , or  $A_{ad} > A_{coh}$ , i.e., in the case where the molecules of the liquid attract the molecules of the other substance more strongly than they do each other, the liquid spreads over the surface.

Harkins defined the coefficient of spreading as being a measure of the attractive force between the molecules of the 2 substances, as

$$S = A_{ad} - 2\sigma_l$$

or

$$S = A_{ad} - A_{coh}$$

or

$$S = \sigma_2 - \sigma_1 - \sigma_{1,2}$$

where  $S$  = the coefficient of spreading of the liquid 1 over substance 2; if  $S > 0$ , the liquid spreads and forms a surface film, whereas if  $S < 0$ , the liquid does not spread but forms drops.

It follows from the aforementioned that only a liquid with a surface tension lower than the surface tension of a given substance can spread over the surface of that substance. The inverse is never the case.

Surface-active substances reduce the surface tension of liquids and thus increase the coefficient  $S$ , or increase the wettability.

Some coefficients of spread on water at 20°C are given in Table 4.3.

TABLE 4.3. COEFFICIENT OF SPREAD  
OF SOME LIQUIDS ON WATER

Liquid	$S$ [erg/cm <sup>2</sup> ]
<u>n</u> -propyl alcohol	49.0
Oleic acid	24.6
Benzene	8.9
Toluene	6.8
Carbon disulfide	- 6.9
Iodobenzene	- 8.8
Paraffin	-13.5

#### 4.2. Adsorption

The surface layer of pure liquids has the same composition as the volumetric phase; on the other hand, the compositions differ in solutions. If the molecules of a dissolved substance are attracted more weakly than the molecules of the liquid, the surface layer will contain more molecules of the dissolved substance than the interior of the solution. This effect can be explained in different ways. For example, the substance whose molecules are attracted with a lesser force also has the smaller surface tension. We know that every structure aspires to an energetic minimum, and that the solutions defined above, aspiring to a lowering of the surface tension, will do so by increasing the concentration of the substance with the lowest  $\sigma$  in the surface layer.

If a substance with a greater intermolecular attractive force, thus with a greater surface tension than the solvent, is dissolved, the dissolved substance concentration is greater in the interior of the solution than in the surface layer.

An increase in concentration in the surface layer is positive (+) adsorption. A lower concentration of the dissolved substance in the surface layer than in the interior of the solution is negative (-) adsorption.

Inorganic electrolytes most frequently exhibit negative adsorption, while most organic compounds exhibit positive adsorption. Surface-active substances always exhibit positive adsorption.

If the adsorption is positive, the concentration in the surface layer is high and the surface tension of the solution is much lower than the surface tension of the pure solvent. If the adsorption is negative, the concentration is low and the surface tension of the solution differs very little from that of the pure solvent.

The dependence between the concentration and the surface tension was stated by Gibbs in 1878.

$$\Gamma = - \frac{a}{RT} \left( \frac{\partial \sigma}{\partial a} \right)_\tau$$

where:  $\Gamma$  = the surface concentration in moles/cm<sup>2</sup>,

$a$  = the activity,

$q$  = the surface area.

For dilute solutions in which the activity is equal to the concentration

$$\Gamma = - \frac{c}{RT} \left( \frac{\partial \sigma}{\partial c} \right)_q$$

where  $c$  = concentration.

The molecules in the adsorption layer always orient themselves perpendicular to the surface, the polar group on the side of the most polar phase. In this manner, homologous compounds with unbranched chains and with polar groups located on the chain ends, because they have equal cross sections, are subject to almost the same

adsorption; also because a mole of each of such substances occupies practically the same surface area

$$\sigma = \frac{1}{N\Gamma_{\infty}}$$

where:  $N$  = the Avogadro number,

$\Gamma_{\infty}$  = the boundary concentration, with maximum packing of the surface by the monomolecular layer.

An effective lowering of the surface tension occurs with low concentrations of surface-active agents up to the formation of the monomolecular layer. Further addition of the surface-active agent provides only minimal changes (Figure 4.2.).

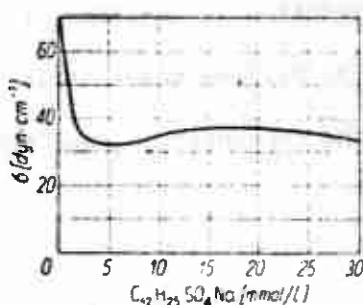


Figure 4.2. The surface tension of an aqueous solution of sodium lauryl sulfate as a function of the concentration at 20°C.

Various surface-active substances provide a maximum lowering of the surface tension at different temperatures.

Compounds with the shortest simple chains and compounds with branched chains or with a polar group which is not on the end of the chain have their greatest ability to lower the surface tension only at temperatures higher than room temperature.

#### 4.3. Dispersion

Dispersion is the state of dissemination of a solid in a liquid. The stability of such suspensions is frequently not great; so-called flocculation takes place -- the scattered particles collect to form larger clusters, which settle to the bottom.

Surface-active agents can counteract flocculation. They are then called dispersing agents. These agents are capable of dispersing substances which have already become aggregated; this process is called peptization.

The following factors are decisive in the stability of a dispersion:

- (1) the size of the dispersed particles,
- (2) the degree of wettability of the solid by the liquid (S),
- (3) the electric charge of the particles.

Obviously, the smaller the particles of the dissolved substance, the greater will be the stability of the suspension and the lesser the sedimentation.

Stability of the dispersion increases the wettability because with increasing coefficient S, the attractive forces between the molecules of the dissolved substance and the liquid increase.

The coefficient S can be increased by employing surface-active agents; in other words, these agents increase the stability of the dispersion, as substances having the greatest ability of being adsorbed also have the greatest stabilizing ability.

Like electric charges accumulated on the surfaces of the dispersed particles cause their mutual repulsion. This counteracts flocculation and aggregation into larger clusters and increases the stability.

## II. SOLID ROCKET PROPELLANT COMPONENTS

Solid rocket propellants are divided into 2 main groups:

- (1) Colloidal propellants, otherwise called rocket powders,
- (2) Composite propellants.

Finally, there is one more group — mixed rocket propellants [35].

Colloidal propellants are colloidal solutions of 2 basic substances: nitro-cellulose and a plasticizer, which is always an aliphatic nitrate of poly-hydroxy alcohols or a nitro compound. Other constituents are present here in minimal amounts. The oxidizer and the oxidized substances cannot be differentiated in these fuels because both constituents are self-oxidizing and, in contrast to most composite fuels, form a homogeneous mixture. These propellants are thoroughly discussed in the work by T. Urbanski [33] and therefore only the most recent achievements in this field, concerning methods of preparation rather than the composition, will be presented here.

Composite fuels have at least several substances in their composition. The most important ones are 2: the oxidizer and the combustible component.

The purpose of the oxidizer is to supply oxygen to the oxidation reaction of the combustible component. We differentiate 2 principal substances in the combustible component: the binder and the plasticizer.

The binder is an organic combustible substance belonging to the polymer group or the petroleum product group; it serves to bind all the propellant constituents together.

Plasticizers are used to provide the appropriate rheological properties during the mixing of the constituents and to obtain the appropriate physical properties after hardening of the propellant. Because plasticizers also act as combustible substances, compounds having a certain amount of oxygen in the molecule (in the form of nitro groups, nitrates or nitrites) are frequently used to improve the oxygen balance.



The following constituents are also found in composite fuels:

- inorganic combustible substances (metals, metal hydrides, metal borohydrides, etc.),
- stabilizers and antioxidants,
- burning rate catalyzers,
- moderators,
- modifiers of the pressure exponent  $n$ ,
- vulcanizers and quaternizing agents,
- surface-active agents,
- polymerization catalyzers,
- agents to lower the ignition temperature,
- hydrophobic substances.

These substances are frequently called "additives".

Additives are present in propellants in small quantities (from hundredths of a part to a few percent) and most frequently, not all at the same time; they play a large part in improving the physical, chemical or ballistic properties of a propellant.

Inorganic combustible substances are used to increase the chemical energy reserves of the propellant. They are finely crushed metals with low atomic numbers, hydrides of these metals, and sometimes borohydrides, carbides, etc.

Stabilizers are usually aromatic amines, some metallic oxides and metallic salts of weak organic acids. They improve the stability of the fuels. The antioxidants, which counteract oxidation of the propellant constituents by the oxidizer during storage, are a variety of stabilizers.

Catalyzers serve to increase the burning rate, while moderators act to decrease it.

Modifiers of the exponent  $n$  decrease its value, whereby the pressure effect on the burning rate is decreased and sometimes this influence disappears altogether.

Polymerization catalyzers, vulcanizers and quaternizing agents permit polymer-

ization and the establishment of a spatial lattice of monomers and polymers.

Surface-active agents lower the surface tension between the oxidizer and the combustible component, which facilitates the introduction of larger amounts of the oxidizer into the fuel. These substances also exert an influence similar to that of stabilizers. Even though they are present in propellants in the amount of hundredths of one percent, they do play a very important role, which is not always duly appreciated.

Hydrophobic substances eliminate the effect of moisture on the constituents of the propellant.

Composite rocket fuels are called heterogeneous fuels by some authors, which is not proper. It is true that most of these fuels actually exhibit a heterogeneous nature; nevertheless, some of them, such as solutions of ammonium nitrate in amines or additive combinations of sodium perchlorate with dimethylsulphoxide, certainly must be included in the composite fuel group (the oxidizer and the combustible substance are different), even though they are completely homogeneous.

As already stated, some authors also assume the existence of a third group of propellants and call them "mixed solid rocket propellants". They combine the elements of the 2 previous groups: oxidizer + nitrocellulose + organic nitrates or nitro compounds. However, this is only a variation of composite fuels by virtue of the fact that the inactive plasticizer fraction is replaced by a self-oxidizing plasticizer and the binder is nitrocellulose.

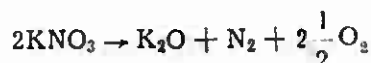
## 5. OXIDIZERS

Solid oxidizers are generally used in the preparation of solid rocket propellants. Liquid oxidizers are almost never considered because of their low stability and large vapor pressures. The oxidizer makes up the major portion of the propellant; therefore, its consistency is decisive in the consistency of the propellant itself.

Both organic and inorganic oxidizers are used, although the latter have a distinct predominance because they are more stable, less sensitive to temperature and much cheaper. One of the basic oxidizers, ammonium nitrate, is mass produced as a chemical fertilizer. Organic oxidizers, mannitol or sorbitol hexanitrate, are based on foods, so they cannot be inexpensive or mass-produced; they are powerful explosives and they constitute a grave danger during technological propellant processes.

The oxidizer must be a substance which, during decomposition, liberates a certain amount of free oxygen, necessary for oxidation of the remaining constituents of the propellant. This oxygen is called "active oxygen" to distinguish it from the total amount of oxygen in the molecule. A portion of the oxygen remains bound in the decomposition products of the oxidizer and is unused.

In the reaction



only 2.5 molecules of oxygen for every 2  $\text{KNO}_3$  molecules are "active", and the oxygen contained in  $\text{K}_2\text{O}$  cannot be considered in subsequent oxidation reactions.

The organic substances of the propellant and the carbon black must be oxidized to gaseous products such as  $\text{H}_2\text{O}$ ,  $\text{CO}$  and  $\text{CO}_2$ .

The greatest thermal effect is obtained by oxidation to  $\text{H}_2\text{O}$  and  $\text{CO}_2$ . However, in this case the mean molecular weight of the exhaust gases increases over the  $\text{H}_2\text{O}$ ,

CO and CO<sub>2</sub> gas mixture, which has an adverse effect on the specific impulse value.

It has been found that the largest impulse is obtained with an amount of oxidizer sufficient to assure oxidation of hydrogen to water and 50% of the carbon to CO and 50% to CO<sub>2</sub>. In order to supply the necessary amount of oxygen, the oxidizer content in solid propellants is 50-90% or more, although its introduction in amounts greater than 75% presents considerable difficulties and a content of 90% is rarely attained. Because the amount of oxidizer is decisive in determining the rheological properties of the propellant, it also influences the choice of charge formation method. With lesser amounts of oxidizer the propellant has such a low viscosity that it can be cast. With larger amounts of oxidizer the propellant must be extruded under correspondingly large pressures. In any case, the percentage by weight of oxidizer is not as important as the percentage by volume.

The specific gravity of the oxidizer is always higher than that of the combustible component; the better the volume ratio, the higher it is. By occupying a greater volume, the combustible component provides the propellant with better physical properties; 50-80% by volume of oxidizer is usually employed [36].

The oxidizer should fulfill many conditions. It should be stable, nonreactive, insensitive to impact at an elevated temperature, at least at the temperature at which the propellant hardens (which is at least 95°C). At the same time it must decompose rapidly at the temperature at which the propellant undergoes pyrolysis. The reaction between the oxidizer and the propellant must be highly exothermic and the activation energy should be high. A high density is desirable not only to increase the ratio of binder volume to oxidizer volume, but also inversely, to increase the weight ratio of oxidizer to combustible component and also to "pack" a large amount of energy in a small volume of propellant, or, in other words, to increase the specific impulse density. The crystals should have a shape as close as possible to the spherical in order to increase the fluidity of the unhardened propellant. They should be of very small size, even of the order of several microns, although much larger ones, up to 0.5 mm, are used.

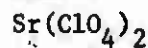
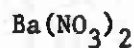
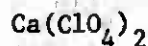
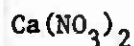
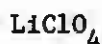
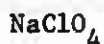
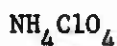
In order to obtain good propellant properties, the oxidizer must be wetted by the combustible component; it must not be hygroscopic or moist. It should be free of phase transformations at the temperatures to which the propellant is exposed during production and storage. It is most preferable if neither the oxidizer nor its decomposition products corrode metals. It is very undesirable and inadvisable if the oxidizer dissolves in the binder because then the propellant decomposition is extremely rapid and its "life" is shortened. Moreover, for military purposes it is frequently desirable that there are no substances in the decomposition products which can cause smoke or fog.

Obviously, there is no ideal oxidizer that would fulfil all the above conditions. Every oxidizer has its good and bad points. Frequently, the addition of certain substances eliminates or reduces the imperfection in the oxidizer; this will be discussed more thoroughly later.

### 5.1. Inorganic Oxidizers

The most frequently used inorganic oxidizers are: nitrates and perchlorates of ammonium, alkali metals and alkaline earth metals.

The most important of these are:

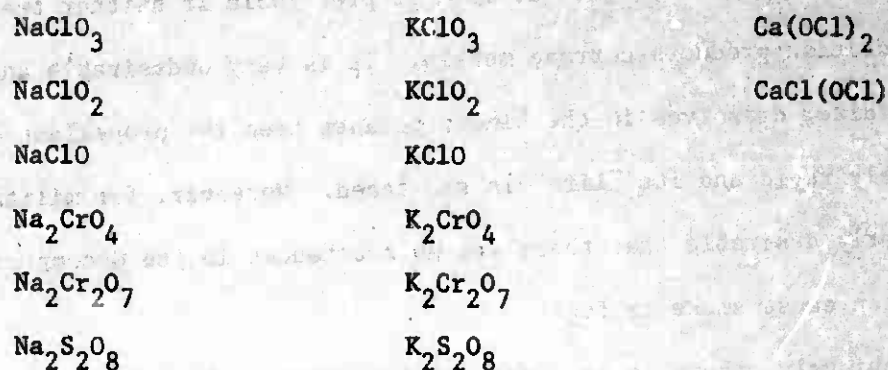


[37, 38, 39]

in addition to hydrazine nitrate ( $\text{H}_2\text{N}-\text{NH}_2 \cdot \text{HNO}_3$ ) and hydroxylamine ( $\text{H}-\text{O}-\text{NH}_2 \cdot \text{HNO}_3$ ) [40].



In the case of combustible components with a small oxygen deficiency, oxidizers with low active oxygen contents, such as chromates, dichromates, chlorates, chlorites, hypochlorites, persulfates, etc., can also be used [41].



Magnesium and aluminum salts can also be used.

Oxidizers with large active oxygen contents are used to oxidize combustible components with small oxygen contents. If the combustible component contains so much oxygen that a vigorous oxidizer could cause explosive ignition, the safest procedure is to use oxidizers with a small active oxygen content.

TABLE 5.1. THE PHYSICO-CHEMICAL PROPERTIES OF THE MORE IMPORTANT OXIDIZERS [42]

Compound	Mol. wt.	Density [g/cm <sup>3</sup> ]	Decomposition reaction	Heat of decomposition		Active oxygen [%]
				kcal/gmol	kcal/kg	
$\text{NH}_4\text{NO}_3$	80.10	1.71	$2\text{NH}_4\text{NO}_3 = 4\text{H}_2\text{O} + 2\text{N}_2 + \text{O}_2$	+29.6	+345	20
$\text{NH}_4\text{ClO}_4$	117.50	1.89	$2\text{NH}_4\text{ClO}_4 = \text{N}_2 + 3\text{H}_2\text{O} + 2\text{HCl} + 2\frac{1}{2}\text{O}_2$	+31.2	+266	34.2
$\text{KNO}_3$	101.10	2.08	$2\text{KNO}_3 = \text{K}_2\text{O} + \text{N}_2 + 2\frac{1}{2}\text{O}_2$	-75.6	-748	39.5
$\text{KClO}_4$	132.60	2.54	$\text{KClO}_4 = \text{KCl} + 2\text{O}_2$	-7.8	-560	46
$\text{NaNO}_3$	85.0	2.26	$2\text{NaNO}_3 = \text{Na}_2\text{O} + \text{N}_2 + 2\frac{1}{2}\text{O}_2$	-60.5	-713	47
$\text{NaClO}_4$	122.60	2.02	$\text{NaClO}_4 = \text{NaCl} + 2\text{O}_2$	-12.4	-102	52
		(1H <sub>2</sub> O)				
$\text{LiClO}_4$	106.44	2.42	$\text{LiClO}_4 = \text{LiCl} + 2\text{O}_2$	-	-	60.1

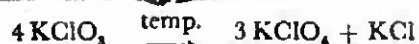
As can be seen from a comparison of the properties of the most important inorganic oxidizers (Table 5.1), only 2 oxidizers, namely, ammonium nitrate and ammonium perchlorate, have positive heats of decomposition; in other words, their decomposition reactions are exothermic. The reason for this is the oxidation of the intramolecular  $\text{NH}_4^+$  group by the oxygen contained in the molecule. A positive heat of decomposition furnishes a considerably greater specific impulse than the utilization of oxidizers with negative heats of decomposition. This is precisely why the 2 above-mentioned oxidizers have the greatest significance; of the 2 ammonium perchlorate has gained predominance, although much intensive work has been carried out to eliminate the imperfections of ammonium nitrate.

#### 5.1.1. Perchlorates

Most inorganic perchlorates are strongly hygroscopic (with the exception of  $\text{KClO}_4$  and  $\text{NH}_4\text{ClO}_4$ ).  $\text{LiClO}_4$  is the best with respect to the active oxygen content, although it is the most expensive. All perchlorates are more expensive than nitrates due to the large consumption of electrical energy required for their production. The basic compound used to obtain almost all the perchlorates is  $\text{NaClO}_4$ .

Perchlorates are obtained by the thermal or the electrolytic method:

thermally from the chlorates, for example



electrolytically by oxidation of the chlorate ion at the anode



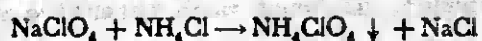
#### Ammonium perchlorate

As already stated, ammonium perchlorate is gaining greater and greater significance because it has a rather high melting point, is not subject to crystal transformation until about  $200^\circ\text{C}$ , has a positive heat of decomposition and is not very hygroscopic. Only gaseous products are evolved during decomposition; thus, no smoke is formed. The active oxygen content (34.2%) is not very high when compared with



sodium or potassium perchlorate; however, this is compensated by the positive heat of decomposition and by the lower mean molecular weight of the exhaust gases. This is accurately reflected in the specific impulse values, which are greater for a given combustible component when ammonium perchlorate is used -- for  $(C_2H_2)_n$ , 250 sec -- than for potassium perchlorate; 210 sec (approximate theoretical calculations for the polymer  $(C_2H_2)_n$  with a large  $n$  number).

The production method is based on the double decomposition reaction in aqueous solution



Because ammonium perchlorate is less soluble than sodium perchlorate at room temperature, equilibrium shifts to the right due to the precipitation of ammonium perchlorate from solution.

The solubility of  $NaCl$ ,  $NH_4ClO_4$  and  $NaClO_4$  in water (g/100 g of water) is

	0°C	25°C	75°C	100°C
$NH_4ClO_4$	11.9	24.9	64.0	
$NaCl$	35.6	35.9	37.7	
$NaClO_4$	62.37	67.8	-	76.7

At higher temperatures the solubility of perchlorate is greater than that of sodium chloride; therefore, primarily  $NaCl$  precipitates out.

The physical characteristics of  $NH_4ClO_4$  are:

mol. wt.	117.50	enthalpy $\Delta H^\circ_{298}$	= -69.42
density g/ml	1.952	molar refraction	17.22
mp with decomposition	450°C	refraction	1.4868

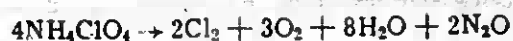
The mean molecular weight of the combustion products is 24.5; the specific impulse attained at  $70.3 \text{ kg/cm}^2$  with reference to 1 atm for the propellant  $(C_2H_2)_n$  is 250 sec. The exponent  $n$  is less than 0.8 for many combustible components with a burning rate of 0.51-2.54 cm/sec for pressures of 14-140  $\text{kg/cm}^2$ . The temperature

coefficient of the pressure is low also; it is possible to reach a plateau. The solubility in g/100 g of solvent at 25°C is given in Table 5.2.

TABLE 5.2. THE SOLUBILITY OF AMMONIUM PERCHLORATE  
IN ORGANIC SOLVENTS, IN g/100 g AT 25°C

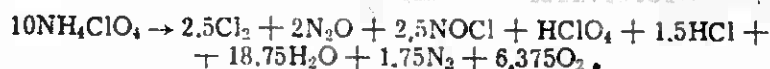
methanol 6.862	<u>n</u> -butanol 0.0170	ethyl acetate 0.032
ethanol 1.907	<u>i</u> -butanol 0.1272	ether (insoluble)
<u>n</u> -propanol 0.3865	acetone 2.260	

The temperature of transition from the rhombic to the regular structure is 240°C.  $\text{NH}_4\text{ClO}_4$  crystallizes from water as an anhydrous salt. There are no known hydrates. However, it does form the triammoniate, unstable at room temperature. Below 300°C decomposition proceeds as follows



and above 300°C the amount of  $\text{N}_2\text{O}$  begins to increase.

Above 350°C decomposition proceeds according to the equation



Gas analysis indicates that  $\text{N}_2\text{O}$  reacts with  $\text{Cl}_2$  and results in  $\text{NOCl}$ . Below 290°C the decomposition is slow and involves only 28-30% of the salt. The following activation energies are observed:

29.6 kcal/mole	below 240°C
18.9 kcal/mole	above 240°C

which are associated with the crystal transformation at 240°C.

At temperatures of 400-440°C, sublimation is more rapid than decomposition. Ammonium perchlorate is more sensitive to impact than ammonium nitrate; it explodes if a 10-kilogram weight is dropped on it from a height of 15 cm. It is easily

ignited in the presence of copper and at the so-called critical moisture content (0.5-0.02%) [2].

#### Potassium perchlorate

This perchlorate occupied the foremost position among the oxidizers before the increased interest in ammonium perchlorate; however, at the present time it is going out of use. Although it has many advantageous properties such as a large amount of active oxygen (46%), a high density, lack of hygroscopicity and failure to melt at low temperatures, it nevertheless does have a number of important disadvantages. During combustion, KCl is evolved, which substantially increases the mean molecular weight of the exhaust gases; a large amount of heat is consumed in fusion and vaporization; and the potassium chloride forms thick white smoke upon condensation. The decomposition reaction is endothermic and absorbs a large amount of heat. As in the case of  $\text{NH}_4\text{ClO}_4$ , it is obtained by a double decomposition reaction



The slightly soluble  $\text{KClO}_4$  precipitates out of the solution.

The physical characteristics of  $\text{KClO}_4$  are:

mol. wt.	132.60	density 2.5298 g/ml
enthalpy	$\Delta H^\circ_{298} = 103.6$	$C_p$ 26.33
molar refraction	15.37	decomp. t. 580°C

The specific impulse attained is 165-210 sec. During decomposition, KCl and  $\text{KClO}_3$  are produced



and form a eutectic, which melts at 556°C. Therefore, decomposition initially takes place in the solid phase, later in the liquid phase.

Table 5.3 gives the solubility in g/100 g of solvent at 25°C.  $\text{KClO}_4$  forms

neither hydrates nor ammoniates. Propellants containing  $\text{KClO}_4$  have a high burning rate (high chemiluminescence of K), 3-6 cm/sec, and a higher combustion temperature than those containing  $\text{NH}_4\text{ClO}_4$ .

Oxidation of carbon black by  $\text{KClO}_4$  proceeds quietly at 320-385°C, whereby the activation energy for the above reaction is  $40 \pm 4$  kcal/mole and is lower than the activation energy for the decomposition of pure  $\text{KClO}_4$  ( $70.5 \pm 0.4$  kcal/mole).

TABLE 5.3. THE SOLUBILITY OF POTASSIUM PERCHLORATE  
IN ORGANIC SOLVENTS, IN g/100 g AT 25°C

methanol	0.1051	n-butanol	0.0045	ethyl acetate	0.0015
ethanol	0.012	i-butanol	0.005	ether	(insoluble)
n-propanol	0.010	acetone	0.1552	ethylene diamine	2.81
methyl amine	1.36	ethylene glycol	1.03	water	2.062

The temperature of crystal transformation from rhombic to isometric structure is 300°C [2].

#### Sodium perchlorate

Sodium perchlorate is very seldom used in rocket propellants because of its high hygroscopicity, even though it does contain a large amount, as much as 52%, of active oxygen. An example of one of its few applications is a propellant-adduct of dimethyl sulphoxide with water and with sodium perchlorate. It is widely used to obtain other perchlorates.

The physical characteristics of  $\text{NaClO}_4$  are:

mol. wt.	122.60	density g/ml	2.5357
enthalpy $\Delta H^\circ_{298}$	= 92.18	molar refraction	13.58
mp	482°C		

It forms the tetraammoniate and the monohydrate. It undergoes a crystal transformation at 308°C. Table 5.4 gives the solubility in g/100 g of solvent at 25°C [2].

TABLE 5.4. SOLUBILITY OF SODIUM PERCHLORATE IN ORGANIC SOLVENTS AND IN WATER, IN g/100 g AT 25°C

methanol	51.355	<u>i</u> -butanol	0.786	ethylene diamine	30.1
ethanol	14.705	acetone	51.745	methyl amine	90.8
<u>n</u> -propanol	4.888	ethyl acetate	9.649	ethylene glycol	75.5
<u>n</u> -butanol	1.864	ether	(insoluble)	water	209.6

#### Lithium perchlorate

This perchlorate has a greater density and almost twice the active oxygen content of ammonium perchlorate; thus, the amount of oxygen is 2.2 times greater per unit volume. It is more stable, and fuels containing it have a higher combustion temperature than those containing  $\text{NH}_4\text{ClO}_4$ . It has several disadvantages: during combustion lithium chloride,  $\text{LiCl}$ , is evolved, and this has a high molecular weight. In addition, its vapors form a thick, white smoke upon condensation after escaping from the nozzle. Moreover,  $\text{LiClO}_4$  is hygroscopic; however, no more so than ammonium nitrate.  $\text{LiClO}_4$  is superior to other oxidizers with respect to active oxygen content and specific gravity. When it is used, the highest specific impulse for solid propellants is obtained. However, wide use of this oxidizer is not possible because of small lithium reserves and because there are no minerals rich in lithium.

The best known is lepidolite, which contains only 3.6-4% Li and is rarely found. Therefore,  $\text{LiClO}_4$  can be used only in exceptional, very particular cases.

The physical characteristics of  $\text{LiClO}_4$  are:

mol. wt.	106.44	density g/ml	2.429
mp	247°C	enthalpy $\Delta H^\circ_{298}$	= 9.77

It has a large n exponent.

The maximum specific impulse is 250-300 sec and the heat of hydration is 14.2 kcal/mole.



Its decomposition is not observed until above 400°C. It forms a trihydrate  $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ , the water of which is very difficult to remove. An anhydrous salt is obtained only after 12 hours of drying at 300°C. The di-, tri- and pentaamoniates are also known:  $\text{LiClO}_4 \cdot 2\text{NH}_3$ ,  $\text{LiClO}_4 \cdot 3\text{NH}_3$  and  $\text{LiClO}_4 \cdot 5\text{NH}_3$ .

$\text{LiClO}_4$  occurs in only one crystal form. Table 5.5 gives the solubility in g/100 g of solvent at 25°C [2].

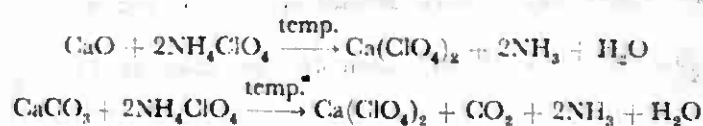
TABLE 5.5. THE SOLUBILITY OF LITHIUM PERCHLORATE IN ORGANIC SOLVENTS, IN g/100 g, AT 25°C

methanol	182.25	i-butanol	58.05	n-butanol	79.31
ethanol	151.76	acetone	136.52	ether	113.72
n-propanol	105.00	ethyl acetate	95.12		

#### Perchlorates of alkaline-earth metals

These perchlorates would undoubtedly be widely used as oxidizers (especially magnesium perchlorate) if it were not for their strong hygroscopicity. In this respect anhydrous magnesium perchlorate even excels above phosphorus pentoxide because it has a greater heat of hydration, but even the hexahydrate,  $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  contains 33.8% active oxygen, or almost as much as  $\text{NH}_4\text{ClO}_4$ .

The perchlorates of the alkaline-earth metals are obtained by heating  $\text{NH}_4\text{ClO}_4$  with oxides or the carbonates



Calcium perchlorate,  $\text{Ca}(\text{ClO}_4)_2$  decomposes as other perchlorates to  $\text{CaCl}_2$ . On the other hand,  $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  yields  $\text{MgO}$  through the  $(\text{MgCl})_2\text{O}$  phase. Because  $\text{MgO}$  has a much lower molecular weight than  $\text{NaCl}$  or  $\text{KCl}$ , and even lower than  $\text{LiCl}$ , it increases the advantages of magnesium perchlorate as an oxidizer.

The enthalpy change of hydration for  $\text{Mg}(\text{ClO}_4)_2$  is  $\Delta H^\circ_{298} = 99.1$ . In addition,

$\text{Mg}(\text{ClO}_4)_2$  forms adducts with methanol, acetone, pyridine, acetonitrile, nitromethane and others [2].

### 5.1.2. Nitrates

Nitrates are among the most inexpensive oxidizers. The most important of these, such as  $\text{NH}_4\text{NO}_3$ ,  $\text{KNO}_3$ ,  $\text{NaNO}_3$  and  $\text{Ca}(\text{NO}_3)_2$ , are widely used as chemical fertilizers; therefore, their production has long been well established. Moreover, some of these compounds occur in the natural state. The use of nitrates as oxidizers for solid propellants is advantageous only in the case of  $\text{NH}_4\text{NO}_3$ . The use of  $\text{KNO}_3$  and  $\text{NaNO}_3$  is not indicated because during combustion they decompose to the oxides  $\text{K}_2\text{O}$  (mol. wt. 94.19) and  $\text{Na}_2\text{O}$  (61.99) which have a high molecular weight, which in turn very adversely affects the specific impulse value. Moreover, these oxides escape in the form of thick smoke. With respect to the molecular weight of the oxide and oxygen content,  $\text{Ca}(\text{NO}_3)_2$  is better ( $\text{CaO}$  = mol. wt. 56.08, active oxygen 49%), but both  $\text{Ca}(\text{NO}_3)_2$  and  $\text{NaNO}_3$  are very hygroscopic, as is  $\text{KNO}_3$  to a lesser extent. Moreover, all nitrates except  $\text{NH}_4\text{NO}_3$  undergo endothermic decomposition. The heat of decomposition has a negative value much higher than that of the corresponding perchlorates.

Ammonium nitrate has a distinct advantage over the remaining nitrates and therefore it is the most frequently used nitrate, although hydrazine and hydroxylamine nitrates are also used, not to mention lithium nitrate, which has a high active oxygen content (58%) and a more advantageous molecular weight of the decomposition products ( $\text{Li}_2\text{O}$ , mol. wt. 29.88) than in the case of  $\text{LiClO}_4$  ( $\text{LiCl}$ , mol. wt. 42.40).

#### Ammonium nitrate

This nitrate has a low active oxygen content but a high heat of decomposition (29.6 kcal/mole). Moreover, all its decomposition products are gases with one of the lowest mean molecular weights as compared with other oxidizers. The chief disadvantages of ammonium nitrate are its low melting point ( $169.6^\circ\text{C}$ ), high hygroscopicity.



plicity and its phase transformations. The low melting point frequently causes the ignited propellant to be extinguished through a flooding of the surface by the molten oxidizer which cuts the combustible component off from the reaction zone. In order to avoid this, substances which increase the viscosity of fused ammonium nitrate are added.

In order to eliminate hygroscopicity, certain hydrophobic agents are used. Because they are used for other hygroscopic substances also, they will be discussed separately. On the other hand, phase transformations constitute an individual feature of ammonium nitrate. Although other oxidizers undergo the same transformations, they do so at temperatures much higher than room temperature, which does not affect the quality of the propellant during storage. Ammonium nitrate has several amorphous transformations which are a function of temperature; one of these occurs at room temperature (Table 5.6).

TABLE 5.6 AMORPHOUS TRANSFORMATIONS OF  $\text{NH}_4\text{NO}_3$

Transformation	Crystal structure	temp. [°C]	Heat of transformation [kcal/mole]
V → IV		-18	0.13
IV → III	Rhombic	32.2	0.40
III → II	Tetragonal	84.2	0.35
II → I	Isometric	125.2	0.99

With the transformation V-IV, the volume increases by about 3% and by about 3.5% with the IV-III transformation [43]. The IV-III transformation is an important disadvantage. If the ammonium nitrate in the hardened propellant is in the IV form, the IV-III transformation takes place with an increase in the volume during storage at a temperature of 32.2°C or during functioning of the engine, if subsequent lots (of the propellant surface) are heated above this temperature. High stresses arise, which could cause cracks and a subsequent unstable, even explosive combustion. On

the other hand, this transformation in the surface layer accelerates the combustion. This is the physical factor, already discussed, which reduced the physical strength of the surface, taken into account in the combustion scheme of a propellant containing  $\text{NH}_4\text{NO}_3$  (see 1.2, The Mechanism of Combustion). The IV-III transformation cannot be prevented; however, this problem is solved by different methods. The entire propellant preparation process can be carried out above the transformation temperature, whereby the III-IV transformation takes place after cooling with a decrease in the volume. The nitrate is loosely arranged in bubbles formed in the combustible component and stresses are thus avoided. When the propellant is used, the ammonium nitrate, being heated, passes into phase III and, upon returning, it completely fills the bubbles, thus constituting a continuous solid phase with the combustible component.

Another method is based on elevation of the transformation temperature by a few degrees, which can be done with the aid of certain compounds. Potassium nitrate is of particular significance here. Together with other additives, such as Prussian blue, silica and aluminum oxide, it exhibits a synergic action (i.e., the effect resulting from the addition of 2 substances together is greater than that of the addition of each substance separately). Table 5.7 gives the transformation temperature elevation.

TABLE 5.7. TEMPERATURE VARIATION OF THE IV-III TRANSFORMATION OF AMMONIUM NITRATE UNDER THE EFFECT OF VARIOUS SUBSTANCES

Additives [%]	Temperature of transformation [°C]	$\Delta t$ .
-	32	0
Prussian blue 5	42	10
Prussian blue 4.3 } $\text{KNO}_3$ 5.3 }	48	16
$\text{SiO}_2$ 5	42	10
$\text{Al}_2\text{O}_3$ 5	38	6

It is evident from the table that the addition of Prussian blue with potassium nitrate shifts the transformation temperature up to 48°C, a temperature that is not reached under ordinary storage conditions. Consequently, the IV-III transformation does not take place and no internal stresses arise [44].

The physical characteristics of  $\text{NH}_4\text{NO}_3$  are:

mol. wt.	80.05	enthalpy $\Delta H^\circ_{298}$	= 87.40 kcal/mole
mp	169.6°C	$C_p$ (273-293°K)	3.8
decomp. temp.	210°C	heat of fusion	1.46 kcal/mole
density g/ml	1.725		

the mean molecular weight of the combustion products with the binder  $(\text{C}_2\text{H}_2)_n$  is 21.8.

The specific impulse attained with the binder  $(\text{C}_2\text{H}_2)_n$  is 210 sec.

The flame temperature is 1730-2150°C [1], and the low burning rate is 0.1-0.3 cm/sec at 70 kg/cm<sup>2</sup>.

It is readily soluble in ammonia, in ethanol at 20°C (3.8 g/100 ml), and in methanol at 20° (17.1 g/100 ml). The solubility in water, in g/100 g, is

0°C	- 118.3	20°	- 192	100°	- 871.0
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Ammonium nitrate is primarily used for gas-generating charges due to its rather low specific impulse, low combustion temperature and the non-corrosive properties of the gaseous combustion products. Propellants containing ammonium nitrate are also used for assisted take-offs. Propellants containing amines and ammonium nitrate exhibit a high impulse value on the order of the impulse of ballistite and can also be used for rocket propulsion; they may also be mixed with asphalt.

The use of the related nitrates of hydrazine and hydroxylamine is very problematic due to the melting point, which is still lower than that of  $\text{NH}_4\text{NO}_3$ , even though many authors mention them as solid propellant oxidizers

	$N_2H_4 \cdot HNO_3$	mp	70.7°C
unstable	$N_2H_4 \cdot 2HNO_3$	mp	104°C
	$NH_2OH \cdot HNO_3$	mp	48°C

#### Other nitrates

As already stated, the nitrates of alkali metals and alkaline-earth metals absorb a large amount of heat energy during their endothermic decomposition and also have a high mean molecular weight of the exhaust gases. Therefore, the specific impulse of propellants based on them is also lower than in the case of  $NH_4NO_3$ . Of this group of oxidizers only  $LiNO_3$  is taken into consideration in the designing of high-energy propellants because of its large active oxygen content. The physico-chemical properties of some nitrates are given in Table 5.8.  $LiNO_3$ ,  $NaNO_3$  and  $Ca(NO_3)_2$  are very hygroscopic.

TABLE 5.8. THE PHYSICO-CHEMICAL PROPERTIES OF THE MORE IMPORTANT NITRATES

Compound	Mol. wt.	Density [g/cm <sup>3</sup> ]	mp [°C]	$\Delta H^\circ_{298}$	Cp	Hydrates
$LiNO_3$	68.95	2.38	261	-115.35	37.2 (528-572°K) 29.5	0; 3
$NaNO_3$	85.01	2.261	306.8	-111.71		--
$KNO_3$	101.10	2.109	334	-118.08		--
$Ca(NO_3)_2$	164.10	2.36	561	-224.05		0; 3; 4

$LiNO_3$ ,  $NaNO_3$  and  $Ca(NO_3)_2$  are very hygroscopic

#### 5.1.3. Other inorganic oxidizers

Oxidizers such as chromates, dichromates and polychromates are used as additives for other oxidizers in amounts up to 10%. Because they have the ability to increase the burning rate, they will be discussed with the combustion "catalyzers".

The persulphates have a low active oxygen content and a high molecular weight

of the combustion products (e.g.,  $K_2O$  and  $SO_2$ ); consequently, they are little used.

Chloric acid salts explode more readily at elevated temperatures than the perchlorates, they contain less active oxygen and are not very stable (ammonium chlorate decomposes at room temperature, resulting in self-ignition after a certain period of time).

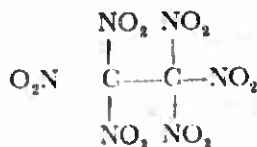
Chlorites and hypochlorites can be used if an inexpensive oxidizer with a low active oxygen content is desired.

## 5.2. Organic Oxidizers

Organic oxidizers do not occupy as important a position in solid propellant production as the inorganic ones. Production of most organic oxidizers is very costly. Some of them, mannitol hexanitrate, for example, are obtained from the processing of food products; others, such as hexanitroethane, require several costly production steps.

Aside from the cost, organic oxidizers are not very stable, especially in mixtures with other combustible components. They are very sensitive to impact and temperature elevations. Most frequently, they are used as additives for colloidal fuels and in composite fuels, mixed with inorganic oxidizers.

### 5.2.1. Hexanitroethane



mol. wt. 300.07

mp 142°C

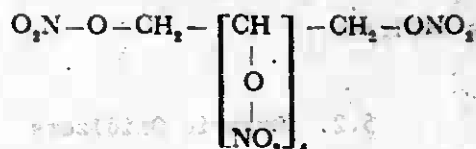
It is obtained by the action of nitric acid on the potassium salt of tetranitroethane.



The amount of active oxygen is high: with complete gasification -- carbon oxidized to CO -- it is 53.3%; and it is 42.6% in the transformation of carbon to CO<sub>2</sub>.

Hexanitroethane is less explosive than picric acid, is not very stable and begins to decompose at 75°C.

#### 5.2.2. Mannitol hexanitrate



mol. wt. 452

needles with mp of 112-113°C

sp. gr. 1.604

It is obtained by the nitration of mannitol with nitric acid in the presence of sulfuric acid.

Pure nitromannite is quite stable (similar to nitroglycerin). It dissolves in ether and boiling alcohol; it is insoluble in water. It explodes from the impact of a 2 kg weight dropped from a height of 4 cm. With gasification to CO, the active oxygen content is 28.3%.

#### 5.2.3. Other organic oxidizers

A number of new organic substances that serve as explosives have recently been obtained. Some of them have a positive oxygen balance and can be used as oxidizers. However, most of them fall short of the oxygen content required for complete gasification. Because they have a high oxygen content in the molecule and a high heat of decomposition, they are suitable as "catalyzers" of combustion that serve to increase the burning rate and improve the oxygen balance of the constituents of the solid propellants.

In summarizing, it must be stated that there is not much progress in the oxidizer field; most of the compounds now in use were already known in the last century. The reason for this state of affairs is the fact that the major emphasis has been placed on obtaining new binders, while oxidizer development has been neglected.



In recent years studies have been undertaken in this field in many lands, particularly on organic oxidizers and binders that can also serve as oxidizers.



## 6. COMBUSTIBLE COMPONENTS

The combustible constituents include the binders, inorganic combustible components, plasticizers and some fillers. All require special discussion except the latter, which are seldom-used substances such as wood flour, grain flour or natural resins, whose properties and composition are individual characteristics. Carbon black is also used as a filler; the different types of this substance will be discussed with respect to its influence on the burning rate.

### 6.1. Binders

In substance, the binding constituents can be almost any known polymer, polycondensate or natural resins, waxes, rubbers, petroleum processing products (tars, pitches, asphalts, etc.).

Their purpose is to bind all the propellant constituents so strongly that the charge will not crack or become deformed during transport or during the impact caused by ignition of the fuel or from the effect of other mechanical factors. It is also required that the grain not be capable to flow during long storage periods.

A condition on the usefulness of a binder is a large hydrogen content in relation to carbon, low nitrogen and sulfur (it is better if there is no sulfur at all). In addition, it is desirable if the binder is not brittle, can wet the other constituents well and has a low viscosity during the propellant production process. In the finished propellant the binder should have a very high viscosity or it should not exhibit the properties of a liquid at all.

The following substances are used: polybutene, polybutadiene, polyisobutylene, polyethylene, polymethacrylates, nitropolymers, polyurethans, polyamides, polyesters, polyacrylonitrile, polystyrene, thiokols, cellulose esters, ethylcellulose, polyvinyl chloride, polyvinyl acetate, nitrated hydroxypolymers, polysiloxates; copolymers, such as polyvinyl chloride-polyvinyl acetate, butadiene-styrene, acrylonitrile-styrene, butadiene-vinylpyridine, etc. Sometimes, brittle resins are

improved by adding plastic ones, e.g., epoxy resins by adding thiokols; styrene, on the other hand, by the polyesters.

Low-melting substances such as tar, pitch and asphalt can be thickened with various inorganic substances to prevent flooding by the non-burning surface. A certain content of oxygen or fluorine (chlorine is not as suitable because of its high molecular weight) atoms in the binder molecules is very beneficial and permits a reduction in oxidizer content. However, a substantial addition of these elements causes a high stability of the compounds and a correspondingly low burning rate. Therefore, teflon is not suitable as a binder.

Furthermore, if a high specific gravity is desired in the case of the oxidizer, a low specific gravity is desired of the combustible components in order to increase the ratio of combustible component volume to oxidizer. If this ratio is small, the propellant can then have inadequate mechanical properties and the method of grain formation is made very difficult; casting is impossible because of the very low fluidity. The weight ratio of the combustible component to the oxidizer is defined by  $\phi$  and is called the mixture ratio

$$\phi = \frac{\text{weight of the combustible component}}{\text{weight of the oxidizer}} \quad (6.1)$$

The stoichiometric mixture ratio  $\phi_s$  is determined for the case of complete combustion as follows

$$\phi_s = \frac{M_{\text{combustible component}} \sum I' v_I'}{M_{\text{oxidizer}} (-1) \sum I v_I} \quad (6.2)$$

oxidizer  
combustible component

where:  $I'$  and  $I$  = the quantities of atoms of the given element in the compound (oxidizer or combustible component),

$v_I'$  and  $v_I$  = valence of the element, taking the sign into account.

If the combustible component is composed of several compounds, it is necessary to calculate the so-called specific equation, in other words, the gram-atom amounts

of the individual elements in 1 kg of combustible component; likewise for the oxidizer. Because such a gram-atom amount  $i$  is equal to

$$i = \frac{1000 \cdot I}{M}$$

by multiplying the numerator and denominator of equation (6.2) by 1,000 and substituting  $i$  and  $i'$ , we obtain

$$\phi_s = \frac{\left( \sum_i i' v_i' \right)_{\text{oxidizer}}}{(-1) \left( \sum_i i v_i \right)_{\text{combustible component}}}$$

where:  $i, i'$  = the number of gram-atoms of the given element in 1 kg of combustible component or oxidizer.

$\phi_s$  gives the combustible component-to-oxidizer ratio, assuming that the total carbon is oxidized to  $\text{CO}_2$ , which, as is well known, is not expedient. Accordingly,  $\phi$  must be somewhat larger than  $\phi_s$ . When half of the carbon is oxidized to CO and half to  $\text{CO}_2$ , a carbon valence value of 3 can be assumed for rough calculations. The  $\phi_s$  value thus calculated is the most advantageous combustible component-to-oxidizer ratio.

The divergence of  $\phi$  and  $\phi_s$  is characterized by the equivalent ratio  $\phi^*$

$$\phi^* = \frac{\phi}{\phi_s}$$

With a deficit of oxidizer,  $\phi^* > 1$ , and with an excess  $\phi^* < 1$ ; it is most desirable that  $\phi^* = 1$ . For most propellants the combustible component content ranges from 50 to 10%, in other words, the value of  $\phi$  is from 1 to 1/9 [7].

There are different ways of preparing propellants. After mixing with oxidizers and other additives, the monomeric liquid binder is subjected to polymerization by the addition of appropriate catalyzers. Some (phenol) resins are thermosetting, while others, such as polyvinyl chloride, the polyacrylates, polyethylene or asphalt, are thermoplastic. Several do not harden but remain soft and elastic, e.g.,

polyisobutylene.

It is necessary that the hardening temperature be low, preferably ambient temperature, which is understandable in view of the resulting reduction in thermal stresses. It is necessary that large volume variations do not occur as a result of polymerization or hardening and that gaseous products are not evolved in order to avoid internal stresses and gas bubbles. In order to attain this, it is necessary to use monomers with large molecules or, preferably, liquid polymers with large molecules, capable of further polymerization or polycondensation. Spontaneous crystallization, which can cause cracking of the grain, is undesirable. The binder should not dissolve the oxidizer because then the propellant is subject to rapid ageing.

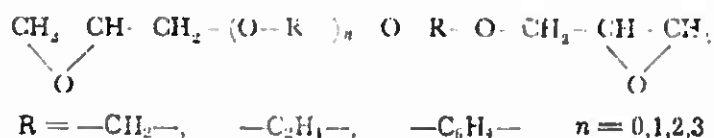
In order to improve the oxygen balance, an attempt is often made to introduce nitro groups into the monomers; however, they have an inhibitory effect on the polymerization process and in many cases the polymerization of nitromonomers is impossible. Consequently, the inverse method is used -- nitration of the finished polymers; however, the introduction of large amounts of nitro groups is not possible by this method. The esterification of polymers with a large hydroxyl group content by means of nitric acid yields better results. Nitropolyurethans can be quite readily obtained. They furnish a large specific impulse, but the presence of nitro groups tends to decrease the stability; thus, the ageing process is more rapid.

The binder itself in composite fuels and colloidal propellants sometimes presents a colloidal composition. The huge nitrocellulose or cellulose acetate molecules form colloidal solutions in plasticizers. Solidification of a propellant of this type depends on the appearance of a gel structure; therefore, after the destruction of this structure, these propellants can be extruded at high pressures and elevated temperatures, and the original consistency will return during the cooling process.

### 6.1.1. Epoxy resins improved with polyamides or thiokols

Epoxy resins have a very important characteristic -- an excellent ability to bind many porous and nonporous materials, which is utilized in particular in binding the individual propellant constituents together. However, once hardening has begun, this process is rapidly completed and they become brittle upon ageing; this immediately limits their use as a binder of solid propellants unless additives are introduced to improve their mechanical properties. The additives can be a whole series of polymers, such as polyamides, polyesters, polyvinyl acetate and thiokols. The thiokols and the polyamides have proved to be the best. The copolymers formed with them have excellent binding properties and, furthermore, retain their elasticity within wide temperature ranges ( $-50^{\circ}\text{C}$  to  $80^{\circ}\text{C}$ ), which is not the case (particularly at low temperatures) for other resin types.

Epoxy resins are used in the form of liquid condensation products of epichlorohydrin with aliphatic or aromatic alcohols. They are diglycidyl polyethers. In the case of 1,2-epoxy-3-chloropropane they are compounds of the type:



Condensation proceeds in the presence of NaOH or  $\text{BF}_3$  [107]. The liquid condensate is subjected to hardening. Resins with the most divergent mechanical properties can be obtained as a function of the condensate composition, hardener type, time and temperature of hardening.

Other epichlorohydrins used are: 1,2-epoxy-4-chlorobutane; 1,2-epoxy-8-bromoacetate; 2,3-epoxy-5-chlorododecane; 5,6-epoxy-7-bromoeicosane.

Aromatic and aliphatic alcohols are both used for condensation. The aliphatic alcohols have 2-20 carbon atoms and 2-3  $-\text{OH}$  groups in the molecule. Among others, they are: ethylene glycol, glycerine; 1,8-dihydroxyacetate; 1,3,5-trihydroxydodecane; 1,2-dihydroxyeicosane; diethylene and hexaethylene glycol. The aromatic

alcohols are: resorcinol, pyrocatechol, hydroquinone, ethylresorcinol, ol(4-hydroxyphenyl)methane (appearing under the name of Bisphenol F); dimethyl-di(4-hydroxyphenyl)methane (Bisphenol A); 2,2-di(4-hydroxyphenyl)butane; 1,5-dihydroxynaphthalene; 3,3-di(p-hydroxyphenyl)valerianic acid; 1,8-di(p-hydroxyphenyl)pentadecane.

However, aliphatic alcohols with 2-12 carbon atoms and 2 -OH groups in the molecule are best for condensation. Condensates with these alcohols have the greatest force of cohesion.

It can happen that the condensation products have too high a viscosity, which would be a drawback in subsequent operations. In this case, solvents are used, which also have the ability of entering into the reaction during hardening. These are substances related to the above-mentioned condensation products, as, for example, allyl glycidyl ether, butyl glycidyl ether, phenyl glycidyl ether (the products of the reaction of 1 mole of 1,2-epoxy-3-chloropropane with 1 mole of the corresponding allyl, butyl or phenyl alcohol).

The hardeners for epoxy resins are primary, secondary and tertiary amines, e.g., ethylene diamine, ethylene triamine, triethylene tetramine, methylene dianiline, *m*-phenyl diamine, 4,4'-diaminodiphenylsulphone, dimethylaminomethyl phenol; liquid polyamides with the -NH<sub>2</sub> and -COOH groups; acid anhydrides, e.g., phthalic, hexahydro phthalic, dodecylsuccinic, boron trifluoride complexes with amines; liquid organic polysulfides (thiokols).

Hardeners of active resins such as dimethylaminomethylphenol are used to the extent of 2-3% while hardeners of polyamides are used 30-50%.

Liquid polyamides -- the products of reactions between dimers or trimers of oleic acids and diamines or triamines (ethylene diamine, diethylene triamine), have proved to be the best for copolymerization with epoxy resins. Other polyamides that are useful here are the condensation products of the following constituents:

(a) Polycarboxylic acids with 2-36 carbon atoms in the molecule: oxalic, malonic, succinic, adipic, cetylmalonic; fumaric, maleic, allylmalonic, dilinoleic



(dimer); phthalic, 1,3,5-benzenetricarboxylic, ethylphthalic.

(b) Amines with at least 2 amino groups possessing at least one hydrogen atom at the nitrogen atom. They can contain 2-5 amino groups and 1-25 carbon atoms, e.g., ethylene diamine, trimethylene diamine, tetramethylene diamine, hexamethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, phenylene diamine, 2,2-di(p-aminophenyl)propane.

(c) Urea derivatives

$R_1-NH-CO-NH-R_2$   $R_1, R_2$  -- H, hydrocarbon chains with 1-12 carbon atoms; for example: methyl urea, ethyl urea, tertiary butyl urea, sym-dimethyl urea, sym-diethyl urea, N-ethyl-N'-propyl urea, N-ethyl-N'-pentyl urea, N-propyl-N'-cyclohexyl urea, sym-dioctyl urea, sym-didodecyl urea, sym-diphenyl urea, N-methyl-N'-phenyl urea, N-methyl-N'-naphthyl urea. Urea derivatives with 3-15 carbon atoms in the molecule and with aliphatic substituents are the best. Mixtures of various amines or urea derivatives are also used for polycondensation.

In addition to the polyamides, polyester-polyamide copolymers are also used as additives to epoxy resins. Polycarboxylic acid is subjected to partial esterification by a polyhydroxy alcohol; and the resultant polyester, which still contains a certain number of  $-COOH$  groups, is subjected to condensation with a polyamine or a urea derivative. For example, esterification of sebacic acid with polyethylene glycol (mol. wt., 400) is carried out in a molar ratio of 2:1. The esterification product reacts with sym-dimethyl urea, yielding a polyester-polyamide copolymer.

After intermixing the 2 resins -- epoxy and polyamide or polyamide-polyester -- and after introducing the oxidizer and additives, the mixture hardens within a temperature range of 20-90°C, preferably 20-70°C.

Epoxy-polyamide resins, as already stated, exhibit a good breaking strength within a wide temperature range; this is indicated by the example below.

Four resins with the following composition were prepared:



				Weight percent	
A	Araldit	502		50	Araldit 502 - a condensate of epichlorohydrin with di- methyl-di-(p-hydroxyphenyl) methane
	Versamid	125		50	
	Tri(dimethylamino- methyl) phenol			3	
B	Araldit	502		50	
	Versamid	125		50	
C	Araldit	502		60	Versamid 125 - a polyamide with reactive amino groups
	Versamid	125		40	
D	Araldit	502		70	
	Versamid	125		30	

They harden at room temperature. Strips 2.5 mm thick and 13 mm wide were used for the studies. The mechanical properties of these resins are given in Table 6.1.

TABLE 6.1. SOME PROPERTIES OF EPOXY-POLYAMIDE RESINS

Resin	-54°C		26°C		74°C	
	Impact strength [kg/cm <sup>2</sup> ]	Elongation [%]	Impact strength [kg/cm <sup>2</sup> ]	Elongation [%]	Impact strength [kg/cm <sup>2</sup> ]	Elongation [%]
A	218	5	158	78	10	47
B	232	4	197	35	11	32
C	148	4	352	33	42	48
D	86	2.5	337	13	24	46

As can be seen, the best properties are exhibited by resin C with a composition of 60% epoxy resin and 40% polyamide resin.

Epoxy-polyamide resins are particularly well suited for inhibition of the charge surface (the purpose of which is to limit the burning surface) because they achieve an excellent union with other resins as well as with the container walls. At the same time, they retain their elasticity within a wide temperature range; this is advantageous in preventing cracking or detachment of the charge coating

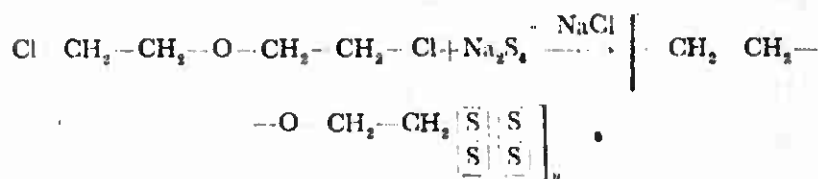
layer. In order to improve the impact strength at temperatures higher than room temperature, fabrics or porous materials formed of polyamide, polyacrylonitrile, methacrylates, polyesters, polyethylene, cellulose acetate, ethyl cellulose, polyvinyl chloride, polystyrene or cotton are impregnated with epoxy-polyamide resins. Such fabrics are frequently applied in several layers. Coatings formed in this manner retain the high adhesion and elasticity of the epoxy-polyamide resins and improve the impact strength at elevated temperatures. They are also very resistant to continuous and violent temperature changes. For example, a strip composed of 3 layers of polyamide fabric impregnated with the above-mentioned resin C and hardened exhibits the following properties [108,109].

	-54°C	27°C	74°C
Impact strength [kg/cm <sup>2</sup> ]	661	633	422
Elongation [%]	36	39	52

Thiokols also bring about marked improvement in the properties of epoxy resins.

Thiokols are the thioplasts which result from the polycondensation of sodium polysulphide with the dichloroderivatives of hydrocarbons, ethers, etc.

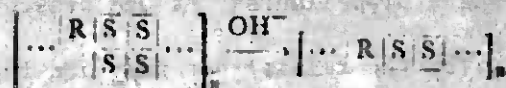
For example, the so-called thiokol B with  $\beta$ ,  $\beta'$ -dichlorodiethyl ether



Both solid and liquid polymers can be obtained, depending on the initial products and the degree of polycondensation.

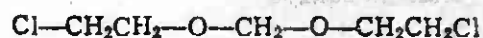
Liquid polycondensates can also be obtained by the partial reduction of solid ones. Then, the long chains end in thiolic -SH groups.

In order to improve the mechanical properties, the thiokols are subjected to desulfurization. The coordinately-bound sulfur atoms are selectively removed by the action of lyes [8].

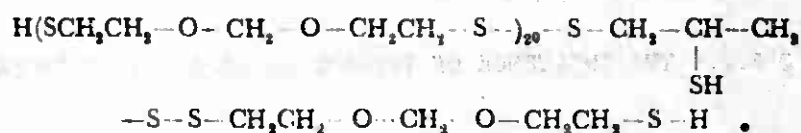


It is better if R is a long hydrocarbon chain because then the percentage sulfur content is reduced; sulfur is inconvenient due to its low calorific value and the formation of combustion products with a high molecular weight ( $\text{SO}_2$  - mol. wt., 64).

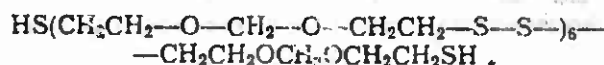
The thiokola designated by LP-2 and LP-3 are the best known. Thiokol LP-2 is a disulfide obtained from dichloro-diethoxy methane (98%)



and from 1,2,3-trichloropropane (2%), which has a suitable space lattice for the purpose. The result is a polycondensate with the schematic formula



Thiokol LP-3 is similar but its molecular weight is only one-third as great:



p-quinone dioxime and  $\text{PbO}_2$  are most frequently used as vulcanizers for these thiokols. Their accelerants are salicylic and maleic acids,  $\text{ZnCrO}_4$ , and diphenyl guanidine. The plasticizers are: furfural, phenol, mono- and dinitropropane, di-(methoxy-ethoxy-ethyl)azelate and o-nitrodiphenyl [45].

Hardening of the liquid thiokols depends on oxidation of the R-SH groups to R-S-S-R. Due to the large linear dimensions of the liquid thiokol molecules, this hardening scarcely results in any volumetric changes at all. It is thus possible to form a grain with very large dimensions (even ~ 4 meters in diameter) without the

appearance of stresses. This is the greatest and most decisive advantage of using thiokols as binders in solid propellants. At the present time, thiokols are generally not used separately (by themselves) but they are improved by combination with other resins, particularly epoxy resins.

Thiokols are capable of forming transverse bonds with epoxy resins, and thus providing good impact strength. The formation reactions of these bonds are catalyzed by amines:

dimethyl-amino-methyl-phenol	DMP-10
tri-dimethyl-amino-methyl-phenol	DMP-30
diethylene triamine	DET
benzyl-dimethylamine	BDA

These amines are used in amounts of 10% in relation to the epoxy resin. A greater elongation, a lower sensitivity to impact and a decreased brittleness [46] are obtained in the polysulfide (Table 6.2).

TABLE 6.2. THE INFLUENCE OF THIOKOL ON EPOXY RESIN PROPERTIES

No.	Thiokol LP-3 in parts by weight to 100 parts by weight of epoxy resin + 10 parts by weight of DMP-30	Tensile strength [kg/cm <sup>2</sup> ]	Elongation [%]	Coefficient of thermal expansion [cm/cm°C·10 <sup>5</sup> ]
1	0	246	0.25	4.5
2	25	387	1	5.5
3	33	457	2	6.0
4	50	506	5	7.5
5	75	216	7	10.0
6	100	165	10	13.5
7	200	10.5	300	15.0

Data for mixtures hardened for 7 days at 25°C

Hardening at room temperature is carried out for 24-36 hours, and the optimal properties are obtained after 7 days. Hardening at 121°C requires about 1 hour.

### 6.1.2. Vinyl-based resins

#### Polyvinyl chloride

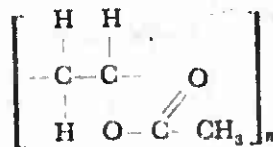


is obtained by the polymerization of vinyl chloride  $\text{ClHC} = \text{CH}_2$ , which can be regarded as an ester of hydrogen chloride and vinyl alcohol. Vinyl chloride is obtained by the action of hydrogen chloride on acetylene in the gaseous phase. The polymerized product is commercially available primarily as a white, powdered substance. Due to the low cost of the raw materials and the simplicity of preparation, it is one of the least expensive polymers.

The best binders for solid propellants are prepared by mixing 1 part by weight of polyvinyl chloride with 1 part by weight of plasticizer. Hardening takes place at 160-175°C within several minutes. In order to increase the durability, it is necessary to add an HCl-absorbing stabilizer because the evolution of even small quantities of HCl can cause polymer decomposition.

Polyvinyl chloride is thermoplastic and its elasticity is retained from -50°C to ~ 60°C. However, it has a significant drawback in the large chlorine content (56%), which very disadvantageously increases the mean molecular weight of the combustion products because of its high atomic weight. Consequently, polyvinyl chloride is used less and less frequently in rocket propellants [37, 47, 48].

#### Polyvinyl acetate



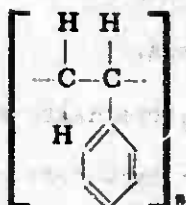
can be used alone as a binder, but it is better in a mixture with other substances



or as a copolymer: for example, with the addition of 28% styrene-acrylonitrile copolymer and possibly also asphalt [49]. However, the copolymer consisting of 10% vinyl acetate and 90% vinyl chloride (Vinylit VYNU, etc.) is more frequently encountered [37,50].

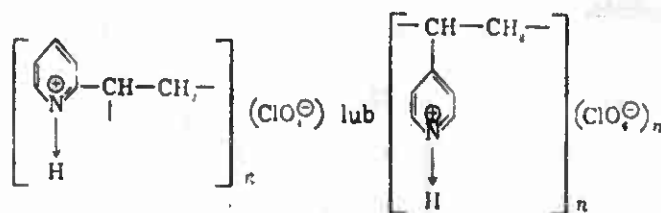
Polyvinyl alcohol nitrate is obtained by the nitration of polyvinyl alcohol in a sulfuric acid solution at a temperature of 40-50°C. The product obtained is readily pulverized and softens at 40-50°C. A maximum of 13.5-14.5% of nitrogen can be incorporated. Polyvinyl alcohol nitrate is inflammable, and it is not very durable. It can be used as an additive for other binders but this is seldom done [36] because it has poor binding properties.

### Polystyrene



Styrene, or vinylbenzene, is obtained by the dehydrogenation of ethylbenzene under a reduced pressure. The polymerization product is thermoplastic but so brittle that it readily lends itself to grinding. It follows from this that polystyrene cannot be used as a binder by itself. On the other hand, numerous copolymers, such as styrene-butadiene, styrene-unsaturated ester, styrene-acrylonitrile, etc., are used.

### Polyvinylpyridine perchlorate

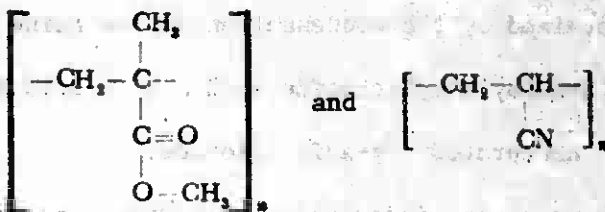


The corresponding polymers, which are not used by themselves, are obtained by

the polymerization of 2-vinylpyridine or 4-vinylpyridine. On the other hand, there are references to the use of the perchlorates of these polymers.

The salt of perchloric acid and poly-2-vinylpyridine is a solid substance with a melting point of 85°C, and it readily burns in an inert atmosphere. This salt is brittle, but it becomes a thermoplastic mass in the presence of nitroglycerin [51].

#### Methyl polymethacrylate and polyacrylonitrile



Methyl polymethacrylate can be used as a binder because it has excellent binding properties, its solutions in plasticizers exhibit a high viscosity and it is resistant to impact. The monomer is readily polymerized by heating, preferably with some polymerization catalyzer (benzoyl peroxide).

Polyacrylonitrile is used less frequently because the monomer is a toxic substance and, consequently, great care must be taken in its polymerization.

Methyl methacrylate and acrylonitrile are both very expensive and, consequently, are not used alone in rocket propellants, but rather as copolymers. They are frequently added in small quantities along with other bonding substances for better propellant particle bonding [52, 53].

#### 6.1.3. Unsaturated amides and urethans

We include the ammonolysis products of acid chlorides, in which at least one reactant has a double bond, in this group. These are amides and urethans, in which the ratio of oxygen to carbon O:C is less than 1:6, and which are expressed by the general formula





where: R-H, alkenyl or alkenoxyl,

R'-H, a lower alkyl, a lower alkenyl or  $\text{-NO}_2$ ,

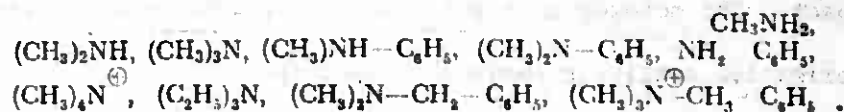
R''-H, a lower alkyl, a lower alkenyl.

Whereby at least one R is unsaturated.

In particular, these compounds are: (1) N,N-dimethylacryl amide, (2) N-methylacrylic amide, (3) N-nitro-N-methylacrylic amide, (4) acrylic amide, (5) N,N-diallylformic amide, (6) vinyl N,N-dimethyl-carbamate.

1, 2 and 5 are obtained by the condensation of the amine with an acid chloride, 3 by the nitration of N-methylacrylic amide with nitric acid and 6 by the reaction of the amine with the unsaturated oxy-acid chloride.

These compounds have a very interesting property. In the monomeric state they dissolve from 5-30% of oxidizers consisting of perchlorate, nitrate and chlorate of ammonium or amines such as:



In this case the dissolved oxidizer is evolved during polymerization in the form of a very fine suspension. The oxidizer introduced into the monomer is then partially dissolved and partially dispersed and consequently can be incorporated in amounts greater than the dissolved amount, which usually constitutes a few percent of the fuel. Because the dissolved fraction precipitates out during polymerization, a propellant prepared in this manner does not contradict the prerequisite that the oxidizer should be insoluble in the binder.

Other unsaturated compounds, such as styrene, methyl acrylate, acrylonitrile, etc., can also be incorporated in the monomer in small amounts. However, oxidizer solubility decreases with increasing content of these compounds. Consequently, the above compounds are not added in amounts greater than 25% with respect to the binder.

Polymerization is carried out at 25-100°C, but preferably below 60°C, utilizing

the commonly used polymerization catalyzers, such as organic peroxides. Table 6.3 presents the properties of ammonium nitrate solutions in monomeric N,N-dimethyl acrylamide.

TABLE 6.3.  $\text{NH}_4\text{NO}_3$  SOLUBILITY IN N,N-DIMETHYL ACRYLAMIDE

N,N-dimethyl acrylamide [%]	$\text{NH}_4\text{NO}_3$	Temperature of solidification [%]
100	0	-25 to -26
96.85	3.13	-27
91.90	8.10	-32
84.94	15.06	do not solidify
81.03	18.97	even at $-75^\circ\text{C}$
75.06	24.94	24.9
74.14	25.86	40

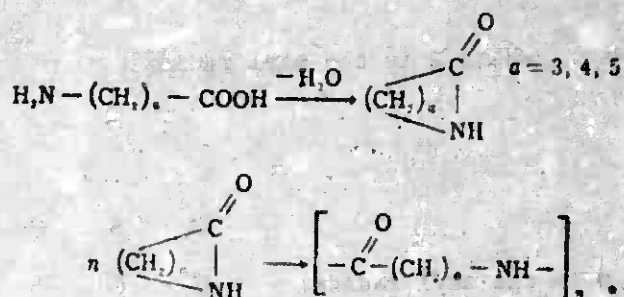
The solubility of ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) in N,N-dimethyl acrylamide at  $25^\circ\text{C}$  is 25%, that of ammonium perchlorate ( $\text{NH}_4\text{ClO}_4$ ), 32%. Moreover, these solutions are readily polymerized [54].

#### 6.1.4. Furfuryl alcohol

A condensate which is capable of polymerization even in the presence of nitro compounds is obtained by the condensation of furfuryl alcohol with the evolution of water. The above capability is a very significant characteristic because the presence of nitro groups renders the polymerization of most monomers impossible. This is one of the few exceptions. Due to this characteristic of the condensate, high-energy nitro-compounds, such as pentaerythritol tetranitrate, hexogen, tetranitrobutane, etc., can be added to the propellant with no adverse effect on the hardening process.

Polymerization of the condensate takes place with the aid of the double bonds of the furan ring under the effect of strong acids, strong bases, or salts of weak

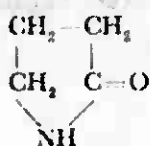
ring and form chain amides



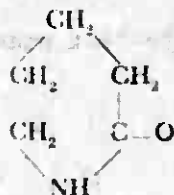
The polyamides and the polylactams have both been mentioned many times as binders for solid propellants. However, both of them are rather costly resins and hence their use is limited.

Lactams with 5-7 members in the ring lend themselves to polymerization. They are readily polymerized even with large contents of anhydrous sodium perchlorate or anhydrous potassium perchlorate at a relatively low temperature in the presence of a basic inorganic catalyzer and with an organic polymerization initiator.

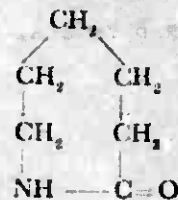
The following lactams are used: pyrrolidone-2, piperidone-2, and  $\epsilon$ -caprolactam



pyrrolidone-2



piperidone-2



$\epsilon$ -caprolactam.

The active catalyzers are the alkali metals and the alkaline-earth metals as well as their derivatives: hydrides, borohydrides, oxides, hydroxides, carbonates and amides. These catalyzers are added in amounts of 0.05-5%, preferably from 0.1 to 1% with respect to the lactam.

Polymerization initiators are N,N-diacyl compounds of the type



polychloroprene.

All these polymers have good elastic properties; however, only carbon and hydrogen (sometimes chlorine) enter into their composition. Therefore, a very large proportion of oxidizer is required for complete gasification (over 80% oxidizer), and with such a content the properties of the propellant become unsatisfactory from the mechanical point of view [56].

Polyisobutylene is suitable for use here because all that is required is to mix it hot with the oxidizer and additives. After cooling, the propellant is ready. However, the high cost of polyisobutylene precludes its use on a large scale, although references to its use in some rockets have been found. For example, the Skylark rocket employs a propellant of composition:

ammonium perchlorate  $\text{NH}_4\text{ClO}_4$

ammonium picrate

polyisobutylene

and has a specific impulse of 177 sec [56, 57, 58].

Polymerized chloroprene is known under the name neoprene. Of course, its use is mentioned only in passing because it is rarely used due to its high chlorine content, which substantially increases the mean molecular weight of the combustion gases [39, 58, 59].

Polybutadiene and other polydienes can be used independently as binders, but, as already mentioned, a stoichiometric amount of oxidizer cannot be incorporated in them. It follows from this that the specific impulses of these propellants will not be high, especially when ammonium nitrate is used, which contains a lesser amount of active oxygen per unit of volume than ammonium perchlorate, and the divergence between the required stoichiometric oxidizer amount and the actual content then increases.

Some sources mention an  $\text{NH}_4\text{NO}_3$  content higher than 80% in fuels with polybutadiene binders (10%) and 10% additives such as combustion catalyzers, carbon black, plasticizer and vulcanizer. They state that about 91% ammonium nitrate is needed for gasification of the polybutadiene fuel.

In order to be able to incorporate stoichiometric amounts of oxidizer, it is necessary to increase the bonding ability of the polydienes. This is achieved by copolymerization with other unsaturated compounds or by the addition of certain types of pitches.

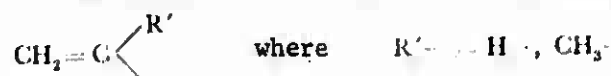
#### 6.1.6. Copolymers of dienes and alkenes with other unsaturated monomers

The most important copolymers are combinations of dienes with vinylpyridine, vinylquinoline and vinylisoquinoline derivatives. These are rubber-like substances which can be vulcanized and have excellent mechanical properties even with large dispersed substance contents. It is not strange that they have recently been classed as the most desirable and "up-to-date" binders; they are superior even to the polyurethans.

The following dienes are used for copolymerization: butadiene-1,3; isoprene; piperylene; methyl pentadiene; 2-methyl butadiene-1,3; 2,3-dimethyl butadiene-1,3; chloroprene; alkoxy derivatives such as 2,3-dimethyl hexadiene 1,3; phenyl butadiene; 2-methoxy-3-ethyl butadiene; 2-ethoxy-3-ethyl hexadiene-1,3; 2-cyano-butadiene-1,3.

Dienes with 4 to 8 carbon atoms in the molecule are most frequently used. Diene mixtures can also be used, e.g., butadiene-1,3 with isoprene.

Heterocyclic N-bases should contain only one group



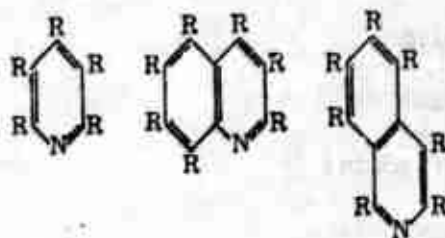
whether it is a vinyl or an  $\alpha$ -methyl vinyl, or an isopropenyl group.

Various heterocyclic N-base derivatives can be used, but the total amount of

carbon in the chains attached to the carbon of the ring can not exceed the number 15 because the polymerization rate decreases with increasing alkyl groups.

Compounds substituted with  $-\text{CH}_3$  and  $-\text{C}_2\text{H}_5$  groups are commercially available.

The heterocyclic N-base derivatives in use are generally represented by the formulas



where R = hydrogen or any of the following groups: alkyl, vinyl,  $\alpha$ -methyl vinyl, alkoxy, halide, hydroxyl, cyanogen, aroxy, aryl and combinations of these groups such as: halide-alkyl, alkyl-aryl, hydroxyl-aryl, etc.

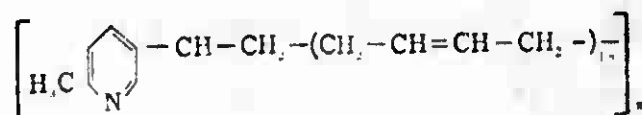
In particular, the compounds are as follows:

2-vinyl pyridine	2-vinyl-5-ethyl pyridine
2-methyl-5-vinyl pyridine	4-vinyl pyridine
2,3,4-trimethyl-5-vinyl pyridine	3,4,5,6-tetramethyl-2-vinyl pyridine
3-ethyl-5-vinyl pyridine	2,6 diethyl-4-vinyl pyridine
2-isopropyl-4-nonyl-5-vinyl pyridine	5-vinyl pyridine
2-methyl-5-undecyl-3-vinyl pyridine	
2,4-dimethyl-5,6-dipentyl-3-vinyl pyridine	
2-decyl-5-( $\alpha$ -methyl vinyl) pyridine	2-( $\alpha$ -methyl vinyl) pyridine
2-vinyl-3-methyl-5-ethyl pyridine	3-vinyl-5-ethoxy pyridine
2-methoxy-4-chloro-6-vinyl pyridine	2-vinyl-4,5-dichloropyridine
2-( $\alpha$ -methyl vinyl)-4-hydroxy-6-cyanopyridine	2-vinyl-4-phenoxy-5-methyl pyridine
2-cyano-5-( $\alpha$ -methyl vinyl) pyridine	
3-vinyl-4-methyl pyridine	



3-vinyl-5-(hydroxy phenyl) pyridine	2-vinyl quinoline
2-vinyl-4-ethyl quinoline	3-vinyl-6,7-di(n-propyl) quinoline
2-methyl-4-nonyl-6-vinyl quinoline	3-vinyl isoquinoline
4-(α-methyl vinyl)-8-dodecyl quinoline	
1,6-dimethyl-3-vinyl isoquinoline	
2-vinyl-4-benzyl quinoline	
3-vinyl-5-chloroethyl quinoline	
3-vinyl-5,6-dichloro isoquinoline	
2-vinyl-6-ethoxy-7-methyl quinoline	
3-vinyl-6-hydroxymethyl isoquinoline	
1-vinyl isoquinoline.	

The most advantageous copolymer is the one with 90% butadiene-1,3 and 10% 2-methyl-5-vinyl pyridine; in other words, there are about 18 butadiene molecules, more or less, for each 2-methyl-5-vinyl pyridine molecule. This copolymer has the following schematic appearance:



although the number of butadiene molecules (or parts of molecules) between the pyridine rings is variable, depending on the instantaneous concentrations and the arrangement of the molecules of the 2 constituents at a given location at the moment of copolymerization.

This copolymer is designated as 90/10 Bd/MVP.

With respect to the quantities of the 2 copolymer constituents, some recommend 75-95% dienes and 5-25% heterocyclic N-bases [39,60], others, 50-95% and 5-50%, respectively [36,61].

It is also possible to use 3 constituents. Then 50% of the diene amount is replaced with styrene, acrylonitrile, etc. [39,60].



Polymerization is carried out in a mass or an emulsion. It is desirable to add up to 35 parts carbon black for each 100 parts of comonomer.

Various vulcanizing or quaternizing agents and hardeners are used to facilitate hardening.

The vulcanizers are the same as those used in natural or synthetic rubbers. Generally, they are sulfur, p-quinone GMP-dioxime, etc. The accelerants are diphenyl guanidine, dithio korbamate derivatives such as Butyl Eight and SA-113, or benzothiazole derivatives, such as NOBS Special; while among inorganic compounds, zinc oxide ZnO and magnesium oxide MgO may be used.

The hardening temperature ranges from 21 to 121°C and, depending on the temperature, the hardening time is from 3 hours to 28 days.

Quaternizing agents are compounds which cooperate with the nitrogen of the pyridine ring or other heterocyclic N-bases. They are alkyl halides, such as methyl iodide, methyl bromide; alkylene halides, such as methylene iodide and ethylene bromide; substituted alkanes, such as chloroform and bromoform; alkyl sulfates, such as methyl sulfate; and others, e.g., benzoyl chloride, methyl benzenesulfonate, benzylidene chloride, benzal chloride, benzyl chloride, hexachloro-p-xylene, etc. [62]. The quaternization temperature used ranges from 0 to 175°C.

It is said that nickel and cobalt salts in the presence of magnesium or zinc oxides are excellent hardeners of copolymers of dienes with heterocyclic N-bases. These salts induce instantaneous hardening if they are used in small amounts. Only water-soluble compounds are effective; thus, chlorides, nitrates, sulfates, etc.

These salts are added in amounts of 0.05-10 (preferably, 0.5-5) parts by weight to 100 parts by weight of the propellant. The hardening time can be regulated from a half minute to 8 hours in a temperature range from 29.5 to 85°C.

It is necessary to form the copolymer before the addition of nickel and cobalt salts because these salts form complex compounds with the heterocyclic N-bases and these complexes do not have the ability to harden.

By way of example, a propellant with a composition (in parts by weight) of

83.5 parts of  $\text{NH}_4\text{NO}_3$ , 16.5 parts of combustible component and 4 parts of  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  hardens instantaneously after the addition of 1 part of anhydrous nickel chloride  $\text{NiCl}_2$  to 100 parts of the mixture. The combustible component of this propellant has the following composition:

- 100 parts of the 90/10 copolymer of butadiene with 2-methyl-5-vinyl pyridine,
- 22 parts of carbon black,
- 20 parts of plasticizer ZP-211 (section 6.3),
- 3 parts of flexamine as the stabilizer (section 7.1.2),
- 3.3 parts  $\text{MgO}$ ,
- 2 parts of Milori blue as the burning rate catalyzer (section 7.2.1).

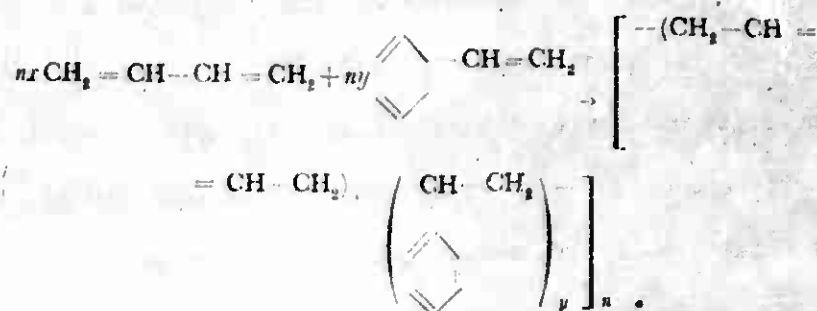
On the other hand, 18 parts of this same combustible component with 82 parts of  $\text{NH}_4\text{NO}_3$  will not harden after 48 hours of heating at  $82^\circ\text{C}$  without a hardener. In a propellant of composition: 18 parts of combustible component, 82 parts of  $\text{NH}_4\text{NO}_3$  and 2 parts of Milori blue, the tensile strength barely doubles after 12 hours of heating at  $82^\circ\text{C}$ . The tensile strength also doubles in a propellant with the composition: 18 parts combustible component, 82 parts  $\text{NH}_4\text{NO}_3$ , 2 parts Milori blue and 0.5 part  $\text{MgO}$ , when heated for 24 hours at  $82^\circ\text{C}$ . A nickel chloride complex with 2-methyl-5-vinyl pyridine, added in the amount of 2 parts to 100 parts of propellant, does not induce hardening after 24 hours at  $82^\circ\text{C}$  (the tensile strength scarcely increases by 1/4).

It is evident from the above that nickel and cobalt salts are excellent hardeners and can be used at room temperature, a feature that is very important with respect to avoiding thermal stresses [63].

Combustible components with copolymers of dienes and N-bases can be improved by the addition of a special type of pitch. Then, larger oxidizer amounts can be incorporated, whereby the propellant retains excellent mechanical properties.

Combinations of butadiene-1,3 with styrene, called GR-S, Buna S, or Buna SS rubber, depending on the ratio of the 2 constituents, are among the other frequently

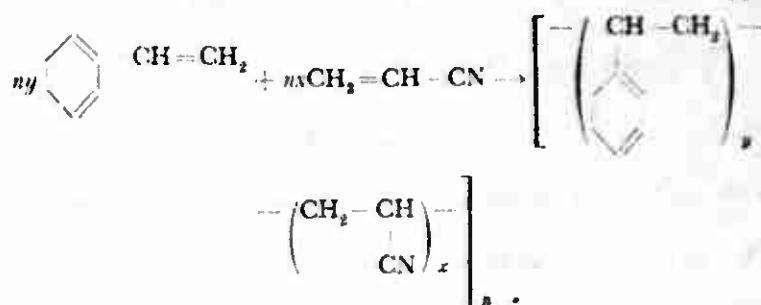
encountered copolymers. This copolymer has the following schematic appearance:



GR-S rubber contains from 1 or 2 to 25% styrene; the best type is GR-S 1505 with a composition of 90% butadiene and 10% styrene. Here copolymerization proceeds readily at a temperature as low as 5°C in the presence of a catalyzer: activated iron oxide.

This copolymer is vulcanized in the same way as other synthetic or natural rubbers. It is used in many rocket propellants [39, 58, 59, 61, 64].

The styrene copolymer with acrylonitrile, frequently modified with asphalt, is also used. It has the following schematic formula:

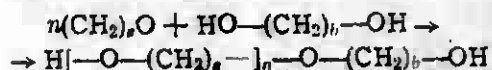


Most frequently, its composition is 15-40 mole % acrylonitrile and 60-85 mole % styrene; most preferably, however, 29 mole % acrylonitrile and 71 mole % styrene [39, 49, 65].

Among the other copolymers used, we should mention isobutylene-isoprene [58], acrylic acid-butadiene (used in the first stage of the Minuteman rocket with oxidizer  $\text{NH}_4\text{ClO}_4$  and with aluminum dust) [66].

### 6.1.7. Polyesters and their copolymers

Polyesters are condensation products of dicarboxylic acids with di- or higher hydroxy alcohols, in which with the most frequently used alcohols the polymerization products (of ethylene oxide or other alkylene oxides with the glycols or the so-called polyglycols) are rich in oxygen (from the ether bonds)



in which  $a, b = 2, 3, 4$  and so on, until the value,  $M = 300-450$ , is reached.

The glycol corresponding to alkylene oxide is most frequently used, and then  $a = b$ .

The esters themselves are not used as binders, but their copolymers with olefins are. In order for this copolymerization to be possible, the polyester should possess a certain degree of unsaturation. This is achieved by the incorporation of a certain amount of unsaturated acids, usually in the amount of 10 to 30% of all the acids used for the polycondensation. The acid dissolves in polyglycol and is heated in 2 stages:

- (a) below  $150^\circ\text{C}$  and (b)  $150-200^\circ\text{C}$ .

At least 70% of the theoretical amount of water should be removed. The amount of water distilled off is a measure of polyesterification progress. The heating lasts for 6-30 hours. The pressure is reduced toward the end.

The molecular weight of the polyester depends on:

- (a) the molar ratio of alcohol to acid,
- (b) the degree of over-reaction (this indicates the amount of water),
- (c) the molecular weight of the alcohol and the acid.

It is most preferable if 80% of the water is distilled off. The greater the alcohol excess, the more complete the reaction. With 20% molar excess of alcohol, the reaction is 85-95% complete. With 30% molar excess of alcohol, it is 90-100% complete. Therefore, a 20% molar excess of alcohol is most frequently used.

The olefin monomer is used in amounts of 1:4 to 1:1 in relation to the polyester. 50% olefin and 50% polyester is most frequently used.

With larger numbers of transverse bonds these resins are thermosetting and with smaller numbers, thermoplastic. The hardening takes place at 104°C. The presence of olefins induces the formation of a space lattice.

The copolymerization catalyzers are: tertiary-butyl hydrogen peroxide, cumene hydrogen peroxide, benzoyl peroxide, lauryl peroxide, acetobenzoyl peroxide, di(t-butyl) peroxide, methyl ethyl ketone peroxide, cyclohexanol 1-hydrogen peroxide, and cycloalkane peroxides. Some catalyzers, such as cyclohexanol 1-hydrogen peroxide and cumene hydrogen peroxide, have the ability of inducing polymerization at room temperature. The catalyzer content is 0.5%.

The polymerization accelerants are cobalt salts, particularly cobalt naphthenate.

A large oxygen content in polyester resins is advantageous in that the stoichiometric amount of oxygen necessary for their oxidation can be achieved with a lower oxidizer content than, for example, in the case of synthetic or natural rubbers. The frequently excessively high brittleness of these resins is a disadvantage, however. Some fractions of saturated liquid polyesters (which have proved to be excellent plasticizers and sometimes also function as surface-active agents) can counteract this imperfection.

The following acids are used for polyesterification: oxalic, malonic, succinic, glutaric, adipic, pimelic, sebacic and citraconic; the unsaturated acids: maleic, fumaric, citraconic, mesaconic, itaconic, etc., and also the anhydrides: itaconic and phthalic.

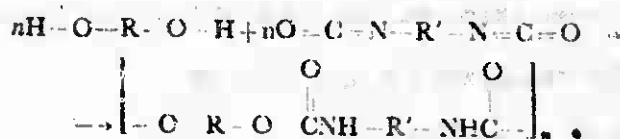
The polyhydroxy alcohols used are: ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, glycerin, erythritol, pentaerythritol, arabinol, adonitol, xylol, mannitol, sorbitol, dulcitol, persitol, wolamitol and the polyethylene and polypropylene glycols.

Olefins which undergo copolymerization with polyesters: primarily styrene,

and then vinyl acetate, the acrylates, the methacrylates, acrylonitrile, diallyl glycolate, diallyl diglycolate, diethylene glycol diacrylate, ethylene glycol acrylate, diethylene glycol diallyl carbonate, diallyl phthalate, diallyl maleate, propylene glycol diacrylate, butandiol-1,3 diacrylate; propylene, butadiene, etc. [5, 67, 68, 69].

#### 6.2.8. Polyurethans

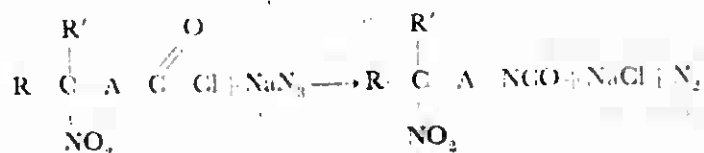
The polyurethans arise from the reaction of diisocyanates with di- or higher hydroxy alcohols, depending on whether linear or spatial polymers are obtained



The diisocyanates are obtained from diamines by reaction with phosgene.

Some American firms have recently synthesized nitropolyurethans. These are polyurethans which were obtained from nitrodiisocyanates or from polyhydroxy nitroalcohols, or from both at the same time.

Nitroisocyanates have a low sensitivity to moisture at room temperature, and they can be obtained by a simpler method than by the reaction with phosgene. It was learned that the nitroacid halides react readily with an aqueous solution of sodium azide with the liberation of nitrogen



A = alkylene,

R = alkyl, carboalkoxyl,

R' = nitro, alkyl, H.

Accordingly, it is assumed that the necessary nitrodiisocyanates are obtained in an analogous manner in the reaction of sodium azide with nitrodicarboxylic acid

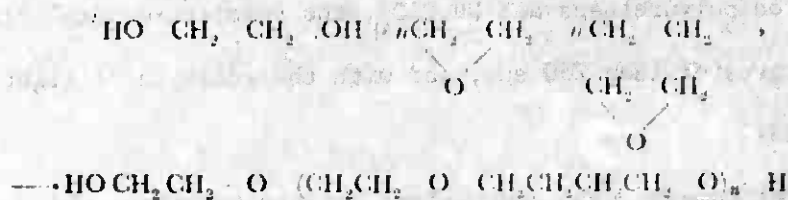


chloride.

When aromatic diisocyanates are used, the nitro groups can appear at the ring.

It has been found that the best polyurethans have long linear molecules and that any branching has an adverse effect. Consequently, polyglycols with straight chains are the most useful. Polypropylene glycol does not comply with this condition because it contains many secondary hydroxy groups.

In order to obtain a suitable polyglycol, the copolymerization of ethylene oxide with tetrahydrofuran in the presence of  $\text{BF}_3$  and ethylene glycol has been carried out in more recent times.



The molecular weight of the diol depends on the amount of catalyzer used: the larger this amount, the lower the molecular weight. For example, with a 1 mole %  $\text{BF}_3$  content,  $\underline{M}$  of the diol = 5290; with 6 mole %,  $\underline{M}$  = 1220. The diol obtained is polymerized with 4,4'-diisocyanate of diphenyl methane. This latter compound also serves to increase the linear dimensions of the copolymer molecules.

In addition to the diisocyanate mentioned, there are references to the use of toluene diisocyanate, which is a mixture of the 2,4- and 2,6-isomers in a ratio of 80:20. Of the linear aliphatic diisocyanates, hexamethylene diisocyanate is used. Obviously, this does not exhaust even an infinitesimal proportion of diisocyanate compounds, and a few data on this subject are required to explain the industrial and State secrecy, because polyurethan binders are greatly superior to most other substances due to their many advantages.

Polyurethans are obtained by mixing diols with diisocyanate and heating with or without a catalyzer, during which time hardening takes place. Depending on the  $\text{-NCO/-OH}$  ratio, the resins range from viscous syrups (for low values) up to rubber-



like products (for high values).

The optimal properties are obtained with an excess of diisocyanates, at least 20 mole %, at the most, 30 mole %. The reason an excess is necessary is probably the partial appearance of diisocyanate dimers during copolymerization with the diol.

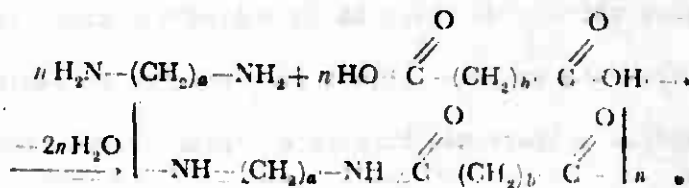
If space lattice formation is necessary, certain amounts of triol are also added to the reaction.

The polyurethans are elastomers that adhere well to container walls, have a good elongation capability and an increased amount of oxygen in the molecule; and they furnish high specific impulses with ammonium perchlorate. For the Polaris propellant based on polyurethans and  $\text{NH}_4\text{ClO}_4$ , the Aerojet-General firm obtained a specific impulse greater than 250 sec, and with the addition of light metals, greater than 270 seconds.

The Aerojet Company also synthesized nitropolyurethan, which can develop a specific impulse of 250 seconds; and with only 65% oxidizer content, it possesses a stoichiometric amount of oxygen. A reduction of the oxidizer amount results in better physical properties of the propellant. However, this improvement is accompanied by a greater sensitivity and a lower chemical stability of the propellant [40, 56, 70, 71, 72, 73, 74].

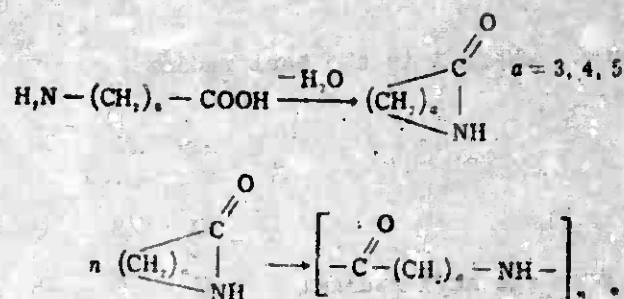
#### 6.1.9. Polyamides and polylactams

Polyamides result from the condensation of polycarboxylic acids with polyamines. Most frequently, one or the other is an aliphatic compound



On the other hand, lactams are already intramolecular amides. They result from the dehydration of the corresponding aminoacids. The molecules thus formed under the influence of appropriate catalyzers have the ability to break the amide bonds in the

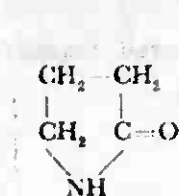
ring and form chain amides



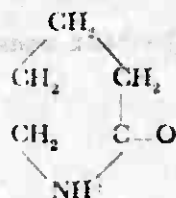
The polyamides and the polylactams have both been mentioned many times as binders for solid propellants. However, both of them are rather costly resins and hence their use is limited.

Lactams with 5-7 members in the ring lend themselves to polymerization. They are readily polymerized even with large contents of anhydrous sodium perchlorate or anhydrous potassium perchlorate at a relatively low temperature in the presence of a basic inorganic catalyzer and with an organic polymerization initiator.

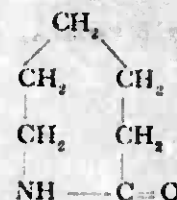
The following lactams are used: pyrrolidone-2, piperidone-2, and  $\epsilon$ -caprolactam



pyrrolidone-2



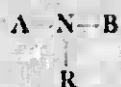
piperidone-2



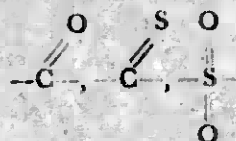
$\epsilon$ -caprolactam.

The active catalyzers are the alkali metals and the alkaline-earth metals as well as their derivatives: hydrides, borohydrides, oxides, hydroxides, carbonates and amides. These catalyzers are added in amounts of 0.05-5%, preferably from 0.1 to 1% with respect to the lactam.

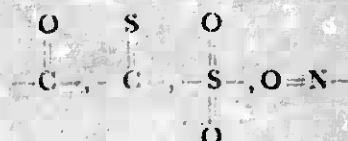
Polymerization initiators are N,N-diacyl compounds of the type



where A is the acyl radical



B is the acyl radical

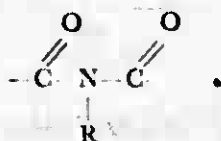


R is either A, or B or the aryl, alkyl, aryl-alkyl, alkyl-aryl, cyclo-alkyl, pyridyl, quinoyl or other groups containing carbonyl, N-substituted carbamyl



alkoxyl, sulfonyl, tertiary amine and other groups which would not react with the lactam or with the polymerization catalyzer.

The A and B radicals can be joined together, forming a ring with the nitrogen (cyclic imides). Sometimes the A radical and tertiary nitrogen can form a ring without the B radical (lactams). The best ones are N-substituted imides with 2 acyl groups



N-acyl lactams, such as N-acetyl-pyrrolidone-2, N-acetyl-ε-caprolactam, N-benzoyl-ε-caprolactam, N-toluoyl-ω-decanolactam, etc., are particularly effective.

Another type of N-substituted imides contains cyclic imides of dicarboxylic acids, for example, N-phenyl succinic imide, N-phenyl maleic imide, N-methyl succinic imide, N-benzoyl succinic imide, N-methyl phthalimide, N-acetyl tetrahydrophthalimide and N-benzoyl phthalimide.

Compounds with larger numbers of tertiary nitrogens are N,N', N''-trimethyl ester of isocyanuric acid and N,N'-di-(phenyl-carbamyl)-N,N'-dimethyl urea.

Other imides are N,N-diacetyl methylamine, N,N-dibenzoyl aniline, triacetamide, N-acetyl-N-formyl ethylamine, N-propionyl saccharin, etc.

The sulfamides are N-acetyl-N-ethyl-p-toluene sulfamide, N-ethyl-N-lauroyl-ethyl sulfamide, N,N-diacetyl-methyl sulfamide, N-(phenyl sulfonyl) succinimide, N-methyl saccharin, N-acetyl saccharin and N-acetyl-N-methyl benzene sulfamide.

The disulfamides are N,N-di(p-toluene sulfonyl) anilide; N,N-di(benzene sulfonyl) methylamine and other N,N-di(benzene sulfonyl) alkylamines and N,N-di(alkyl sulfonyl) alkylamines, for example, N,N-di(methyl sulfonyl) ethylamine.

The N-nitrosoamides are N-nitroso-pyrrolidone-2, N-nitrosuccinimide, N,N-diacetyl nitrosamine, N-nitroso-N-methyl urethan, etc.

The N-nitroso sulfamides are N-nitroso-N-methyl-benzene sulfamide; N-nitroso-N-methyl-p-toluene sulfamide; N-nitroso-N-ethyl-methane sulfamide; N-nitroso-N-phenethyl-butyl sulfamide, etc.

One or more acyl oxygens can be replaced by sulfur without reducing the effectiveness of these compounds, e.g., N-thio-benzoyl pyrrolidone-2; N-thiopropionyl-maleic imide; N-phenyl-dithiosuccinic imide and N-(n-octyl-carbamyl)-thiopyrrolidone-2.

Polymerization initiators are used in amounts of 0.01-5 mole %, better 0.01-2 mole %, best 0.1-1 mole % with respect to the lactam.

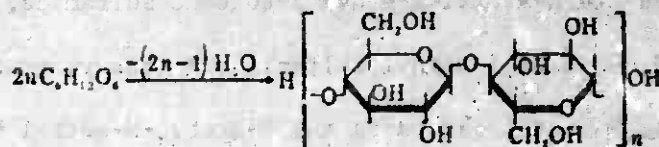
If a polymer with a larger molecular weight is desired, a lower initiator concentration is used.

The entire polymerization process may proceed at a temperature up to 250°C, preferably up to 190°C, and most preferably from 130 to 170°C. For lower-molecular-weight lactams (pyrrolidone) this process can begin to take place at a temperature as low as 35°C [49, 75].



### 6.1.10. Esters and cellulose derivatives

Cellulose is a natural polycondensate consisting of cyclic d-glucose molecules joined (after removal of the water molecules) by ether bonds

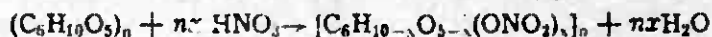


In general, we can assume the cellulose formula to be  $(\text{C}_6\text{H}_{10}\text{O}_5)_n$ , because the H- and OH- chain terminal groups have little significance in view of the enormous molecular weight of cellulose, defined as from 300,000 to 500,000.

There are only 3 hydroxy groups for 6 carbon atoms; accordingly, only a corresponding number of acyl or alkyl groups can be incorporated.

#### Cellulose nitrate (nitrocellulose)

Nitrocellulose results from the esterification reaction of cellulose with nitric acid or with nitrating mixtures or with nitrogen oxides.



where x can have a number of total and fractional values from 0 to 3, corresponding to a nitrogen content (the so-called nitrogen number) or from 0 to 14.15%.

Pure nitrocellulose is chemically stable; but the impure substance, particularly the nitrating mixture, is readily decomposed, is very sensitive to impact and explodes with ease. The cellulose sulfates and sulfate-nitrates which arise during nitration (in the  $\text{H}_2\text{SO}_4\text{-HNO}_3$  nitrating mixture), and some cellulose decomposition and oxidation products contribute to this instability. In order to avoid these adverse properties, the nitrocellulose is subjected to stabilization. The sulfate esters in question readily undergo hydrolysis by boiling in dilute acids during preparation. Thus, the nitrocellulose is boiled in 1%  $\text{H}_2\text{SO}_4$ , then in water, later in a

weakly alkaline solution and finally again in water. The density of the various nitrocellulose types is about  $1.65 \text{ g/cm}^3$ .

Nitrocellulose dissolves in many solvents, depending on the degree of nitration as well as the method of nitration. Colloidal solutions result. Organic and inorganic esters (nitrates, phosphates, silicates), ketones, ethers, aldehydes, alcohols, nitrocompounds and heterocyclic compounds are good solvents.

The viscosity of the solutions depends on the size of the molecules as well as the degree of nitration. Nitrocellulose with a higher nitrogen content has a higher viscosity in solution.

Nitrocellulose burns readily without detonation. An explosion can occur if it is burned in a closed space.

When it is used for colloidal fuels, i.e., the so-called smokeless powders, it usually contains more than 12% N. However, the nitrogen content should not be too high, in order for the nitrocellulose to be capable of dissolving when hot in polyhydroxy alcohol nitrates and forming a homogeneous gel after cooling. In some methods of producing nitrocellulose and nitroglycerin powders, the nitrocellulose must also dissolve in the solvents used. Usually, the most suitable substance is one with a nitrogen content of 12.6%.

The nitrocellulose content varies widely in different propellants, from a low value of 20% to a high value somewhat below 90%.

Explosive substances (nitroglycerin or nitrodimethylene glycol, nitroaromatic and nitroaliphatic compounds) as well as nonexplosive substances (phthalates, organic phosphates, organic silicates and mixtures of them) are used as plasticizers.

Nitrocellulose is an excellent binding agent. It is very elastic when plasticizers are added. It readily binds solid substances and forms a gel of liquid constituents.

The disadvantage of nitrocellulose is the impossibility of casting powder charges due to the fact that colloidal solutions with large nitrocellulose contents have such a high viscosity that it is possible to obtain only grains with small

diameters even by employing extrusion methods. Other methods are based on the use of a solvent, but even in this case it is not possible to form grains of large diameter because it is very difficult to evaporate off the solvent. A new method is similar to that long used for nitrocellulose powders without a plasticizer. This method consists of the introduction of nitrocellulose, nitroglycerin, stabilizers and other additives to an ethyl acetate emulsion in water. During intensive mixing, these constituents dissolve in the ethyl acetate. Then the solvent is distilled off and spherical particles of homogeneous propellant remain in the water. These particles are drained and dried and then molded (by compression) into a grain of appropriate form [6, 53, 67, 76, 77, 78, 79].

#### Organic esters and cellulose ethers

Esters of the lower aliphatic acids and cellulose are frequently used as binders for propellants. The best of these are the acetates, propionates, butyrates, etc. The esters can also be mixed, e.g., acetate-propionates, acetate-butyrate, acetate-sorbates, etc. They are obtained by the action of anhydrides of the appropriate acids on cellulose.

These esters are classified by the percentage of the given acid obtained after hydrolysis and by the viscosity of the 20% acetone solution at 25°C.

The cellulose acetate used contains 51-57% acetic acid, most preferably, 54-56%; the viscosity in acetone at 25°C is 2-80 cp. The best cellulose acetate-butyrate contains 7-55% acetic acid and 16-61% butyric acid and has a viscosity in acetone of 10-40 cp at 25°C.

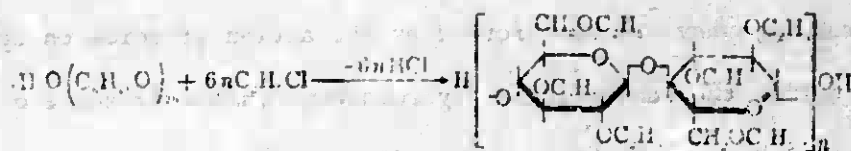
The cellulose ester particles should be spherical or nearly so, with a maximal diameter of 100 microns and be nonporous. The best density is 1.2-1.3 g/cm<sup>3</sup>.

Like nitrocellulose, cellulose esters are capable of forming a gel with the liquid constituents and binding the solid ones. After mixing at a low temperature (preferably 35°C), all the substances entering into the propellant mixture composition are heated to 100-155°C, depending on the composition, whereby the cellulose



ester dissolves in the plasticizer, then gelation begins and the propellant hardens. This process is also possible at lower temperatures, but it requires a much longer time. This is complicated by the fact that the plasticizer diffuses to the interior of the cellulose ester particles, resulting in diminished homogeneity of the mixture. If nitroglycerin is used as the softener, the hardening temperatures cannot exceed 115-120°C. The propellants obtained with cellulose esters have thermoplastic properties.

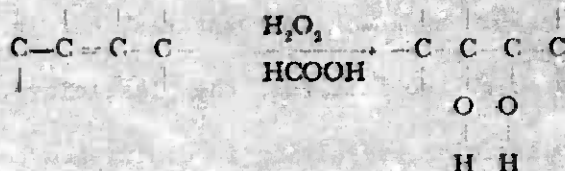
The use of cellulose ethers, the so-called alkyl celluloses, as binders has been mentioned more than once. Alkyl-group derivatives with a carbon atom content of less than 6 are used. Most frequently encountered is ethyl cellulose. Alkyl celluloses are obtained by the action of alkyl chlorides on cellulose



in which the degree of etherification can be different, depending on the reaction conditions and the amount of alkyl chloride. The monoalkyl celluloses are the best [38, 40, 43, 44, 49, 67, 80, 81].

#### 6.1.11. Nitrates of hydroxypolymers

Attempts have long been made to obtain highly nitrated polymers. However, as is well known, nitroalkenes polymerize either very reluctantly or not at all. Consequently, satisfactory results could not be obtained by this method. Recently, investigations have followed another course. Well known and widely used polymers containing double bonds were subjected to hydroxylation by hydrogen peroxide in the presence of a catalyzer (formic acid)



The hydroxy-polymers obtained are subjected to esterification by nitric acid.

The resulting polymer should have a molecular weight of at least 350 and up to 500,000, and sometimes even higher, and the iodine number (Wijs' method) should be 150-625. The molecular weight is determined by the cryometric method in benzene for polymers with a molecular weight of 350-2000 and for those with 2000-500,000 by measuring the osmotic pressure.

These polymers result from the high-boiling fractions after refining or cracking of petroleum; they are also formed by the action of acids on cracked kerosene as well as during the conversion of hydrocarbons in the presence of hydrogen fluoride (the by-products are the ones that dissolve HF), particularly in the reaction of isoparaffin with propylene, butylenes, amylenes and olefin mixtures boiling above 260°C.

Other important olefins are the liquid diene polymers and the copolymers: polybutadiene, polyisoprene; copolymers of dienes with other monomers, such as rubber-like substances with styrene, acrylonitrile, methacrylates, acrylates, etc.

The liquid olefin polymer should have a molecular weight less than 5,000, and it is best if it is less than 2,000. These are liquids with a Saybolt viscosity of 100-6,000 sec at 37.8°C. A polymer of this type can be prepared by the polymerization of 1,3-butadiene using sodium.

Hydroxylation is carried out with hydrogen peroxide or a substance capable of forming it, with or without the presence of a solvent, and with a catalyzer, which may be formic acid or ethyl or methyl formate. The best conditions are a temperature of 10-95°C and a time of 1-60 hours.

It is necessary to hydroxylate at least 10% of the double bonds, preferably

20%; but it should not exceed 30%. Fuming  $\text{HNO}_3$  is mixed with acetic anhydride at a temperature of  $-10$  to  $+10^\circ\text{C}$ . The hydroxy-polymer is gradually added to the mixture. The amount of nitrating mixture is such that at least 25% of the  $-\text{OH}$  groups are esterified and that up to 100% of the  $-\text{OH}$  groups can be esterified.

The polymers thus obtained can be extruded or cast under pressure into forms; they can also be mixed with inorganic oxidizers in amounts of 10-50% polymer and 50-90% oxidizer.

Partially nitrated hydroxypolymers with a relatively low molecular weight can be condensed with compounds such as maleic and phthalic anhydrides or diisocyanates (nitropolyurethane resins are formed). This condensation can be carried out in the presence of an oxidizer [41].

#### 6.1.12. Asphalts and pitches

Products resulting from the processing of petroleum or coal -- various types of tars, pitches and asphalts -- are quite frequently used as binders. Formerly, these substances were used alone as propellant binding agents, with the mere addition of plasticizers (various oils) (GALCIT, the propellant of the Polaris rocket projectile, had the composition  $\text{NH}_4\text{ClO}_4$ , asphalt and oils). However, at the present time they are improved with various polymers. Our attention is primarily drawn to the low cost of these substances and, depending on the production method, the number of excellent properties such as the good binding capabilities, elasticity when cold, plasticity when hot, which facilitates the formation of the charges.

Asphalts are obtained by scavenging the distilled fractions or residues with air after the distillation of petroleum. Asphalts with a softening temperature of  $66.5$ - $149^\circ\text{C}$ , preferably however  $80$ - $107^\circ\text{C}$ ; with a penetration greater than  $0.8$  mm at  $0^\circ\text{C}$  and less than  $4.0$  mm at  $46^\circ\text{C}$  (according to ASTM); and with an ignition temperature lower than  $288^\circ\text{C}$ , are used.

The drawback with asphalt is the flooding of the propellant surface during combustion, which can lead to an extinguishing of the flame. This can be remedied by



adding thickeners; this will result in the asphalt having a high viscosity after melting.

The pitches are especially useful. In some propellants they constitute 50-90% of the binder, preferably 60-80%. There are several methods of producing the appropriate pitches. Their properties depend to a great extent on the method of preparation.

Petroleum is cracked at a temperature of 454-538°C under a pressure of 3.5-10.5 atm. The product obtained is fractionated and the residue is cracked in another cracking unit at a temperature of 482°C and under a pressure of 3.5-28 atm. This is the way the cracking is carried out insofar as it is possible. The residue is placed in a vacuum distilling unit and distilled at 315-482°C and 0.01-20 mm Hg, preferably at 0.01-8 mm Hg. The undistilled substance is the desired pitch.

Another method is as follows. After a weak cracking stage, the product is subjected to distillation, the residue is further cracked and again distilled in a vacuum. In order to reduce the amount of coke, an aromatic solvent is added to the cracking and it is further treated as above.

The pitches obtained have a softening temperature of 88-121°C and a penetration of 0-5 mm at 46°C [100 g in a period of 5 seconds]. They contain 70-75% asphaltenes and 25-30% malthenes. The asphaltenes are insoluble in light hydrocarbons such as n-pentane, cyclopentane, n-hexane, n-heptane, light petroleum, etc.; on the other hand, the malthenes are soluble. Pitches have a high aromatic compound content and are lacking in naphthenes. Asphalts, on the other hand, not having such good properties as pitches, are characterized by a 25-50% asphaltene content, a small amount of aromatic compounds and the presence of naphthenes.

A typical pitch has the following properties:

softening temperature	115.6°C
density at 15.6°C	1.1 g/cm <sup>3</sup>

	t°C	mm
penetration (100 g in a period of 5 sec)	25	0
	37.8	0
	46.1	1
	54.4	2
	65.6	10

		%
solubility	in CS <sub>2</sub>	99.2
	in benzene	97.8
	in CCl <sub>4</sub>	89.3

		%
analysis	C	87.3
	H	7.4
	N	0.23
	S	2.17
	ash	1.28
	water	0.29
	oxygen and others	<u>1.33</u>
		100.00

At present, binders of pitch improved with the copolymer 90/10 1,3-butadiene with 2-methyl-5-vinyl pyridine (this copolymer is denoted by the abbreviation 90/10 Bd/MVP) have the best properties.

A measure of the strength of a propellant with respect to mechanical factors is the cyclic test, based on alternate heating and cooling of the charge, by which it is exposed to great thermal stress changes. The more such cycles tolerated by the propellant, the more suitable it is. In carrying out this study, the grain is subjected to a temperature of -56.7°C for 24 hours, after which the temperature is instantaneously raised to 76.7°C for another 24 hours. This is one cycle. Ruptures appear after several, a dozen or several score of such cycles, depending on the propellant.

The superiority of the binder, pitch + 90/10 Bd/MVP, over pitch alone is indicated by the following data:

	%
Propellant of composition $\text{NH}_4\text{NO}_3$	82.95
$\text{KNO}_3$	9.22
Pitch	4.11 (pitch:Bd/MVP ratio, 70:30)
90/10 Bd/MVP	1.76
$(\text{NH}_4)_2\text{Cr}_2\text{O}_7$	1.96

tolerates 65 cycles while an identical propellant with pitch alone tolerates only 15 cycles.

On the other hand, the superiority of pitch over asphalt is indicated in the data of a number of propellants (Tables 6.4 and 6.5).

It is evident from the above that in spite of crystal transformations of the ammonium nitrate, the propellant with the binder, pitch + Bd/MVP, tolerates as many as 65 cycles, i.e., more than 4 times more than in the best case involving the use of asphalt. It is also worthy of note that the binder amounts to less than 6% of

TABLE 6.4. THE PROPERTIES OF PROPELLANTS CONTAINING ASPHALT AND FORMED BY COMPRESSION MOLDING

Constituents	Composition (%)		
	I	II	III
$\text{NH}_4\text{NO}_3$	82.95	82.95	82.95
$\text{KNO}_3$	9.22	9.22	9.22
Asphalt with a softening point of 76.7°C	5.87	-	4.11
Asphalt with a softening point of 132.2°C	-	5.87	-
90/10 Bd/MVP (containing 20 parts by weight of carbon black and 3 parts by weight of stabilizer per 100 parts by weight of copolymer)	-	-	1.76
$(\text{NH}_4)_2\text{Cr}_2\text{O}_7$	1.96	1.96	1.96
Number of cycles	15	5	10



TABLE 6.5. THE PROPERTIES OF PROPELLANTS CONTAINING ASPHALT OR PITCH FORMED BY THE METHOD INVOLVING SOLVENTS

Constituents	Composition (%)	
	IV	V
$\text{NH}_4\text{NO}_3$	82.95	82.95
$\text{KNO}_3$	9.21	9.21
Pitch with softening point of 115.6°C	3.92	-
Asphalt with softening point of 132.2°C	-	3.92
90/10 Bd/MVP	1.96	1.96
$(\text{NH}_4)_2\text{Cr}_2\text{O}_7$	9.96	1.96
Number of cycles	65	10

of propellant.

The following can be used in a mixture with pitch instead of Bd/MVP: polybutadiene, polyisobutylene, isoprene, the copolymer isobutylene + isoprene, copolymers of dienes with styrene, etc.

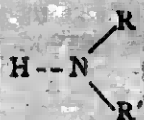
Asphalt is used in a mixture with the copolymer styrene + acrylonitrile (15-40 mole % of acrylonitrile) in ratios of 70:30 to 10:90, or from 10 to 70%, preferably from 33 to 66% [44, 49, 52, 58, 65, 71, 82].

#### 6.1.13. Other substances

As already mentioned, there are propellants -- either solutions, such as  $\text{NH}_4\text{NO}_3$  in methylamine, or mixtures, such as hexogen with nitroguanidine -- in which the oxidizer and the combustible component cannot be distinguished.

#### Amines

It was learned that methylamine and other amines form solutions with ammonium nitrate. Thus, there are a number of compounds with the formula



where: R = alkyl, hydroxyalkyl or  $-\text{C}_2\text{H}_4\text{NH}_2$

R' = hydrogen, alkyl or  $-\text{C}_2\text{H}_4\text{NH}_2$

The physical properties of  $\text{FH}_4\text{NO}_3$  solutions in  $\text{CH}_3\text{NH}_2$  are given in Table 6.6.

TABLE 6.6. SOME PHYSICAL PROPERTIES OF  $\text{NH}_4\text{NO}_3$  SOLUTIONS IN  $\text{CH}_3\text{NH}_2$

Physical properties	Units	$\text{CH}_3\text{NH}_2$ [%]	
		18.1	27.1
$n_D^{25}$ - coefficient of light refraction	-	1.4462	1.4344
Density at temperature 15°C	g/ml	1.2434	1.1504
" " " 25°C		1.2397	1.1463
Viscosity at temperature 10°C	cp	-	7.8
" " " 15°C		11.47	6.9
" " " 20°C		10.06	6.2
" " " 25°C		8.86	5.5
" " " 30°C		7.96	5.0
Vapor pressure at 40°C	mm Hg	567	1,126
" " " 30°C		375	763
" " " 20°C		-	691
" " " 10°C		243	447
" " " 0°C		176(+0.9°)	333
" " " -30°C		44	79
Freezing (solidification) point	°C	17	1.8
Ignition temperature		400-450	400-450

Let us turn our attention to the universality of the use of  $\text{NH}_4\text{NO}_3$  solutions in  $\text{H}_3\text{C-NH}_2$ . Solutions with 2-6% methylamine content are solid and, with various

additives such as aluminum dust, carbon black, etc., they can perform as solid propellants for projectiles and rockets. Mixtures with 6-15% methylamine have the consistency of mud or sludge and can be employed as single-constituent liquid fuels. With contents of 15 to 40%, they are liquids used for two-component propellant engines. Solid and sludgy mixtures are comparable with ballistite with respect to both the specific impulse and the density and escape velocity.

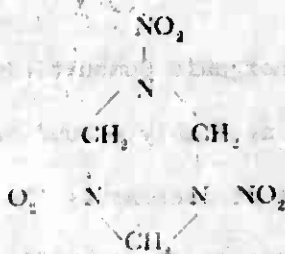
With a lower methylamine content, the explosive properties come to the fore. 5-10% solutions are most sensitive to impact. Liquid solutions have the same order of sensitivity to impact as pure  $\text{NH}_4\text{NO}_3$ . 6-15% mixtures have a specific impulse higher than 200 seconds and a specific density impulse  $\sim 300$  seconds.

The density of granulated  $\text{NH}_4\text{NO}_3$  used for explosives is equal to  $0.90 \text{ g/cm}^3$ . The density rises to 1.5 through the addition of 7.0-8.0% methylamine. This density rise increases the sensitivity of the charge to impact.

A very positive feature of solutions of the above type is the high stability with respect to chemical properties, without the use of stabilizers. Nevertheless, the physical stability is not great due to the high vapor pressure of methylamine over these solutions, which arises from the properties of the methylamine itself. Its boiling point is  $-6.5^\circ\text{C}$ ; consequently the charge must be protected against a methylamine loss [83,84].

#### Hexogen with nitroguanidine

Hexogen is cyclotrimethylene trinitroamine.



It is an explosive material with a rather high sensitivity to impact (2 kg from 30-32 cm). It is a white, crystalline substance which exothermically

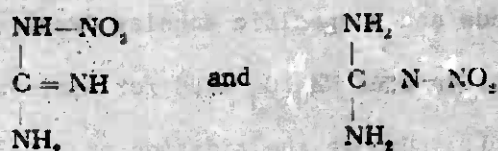


decomposes (21.3 kcal/mole).

By itself, compression-molded hexogen does not have great mechanical strength. On the other hand, it has been observed that it acquires a high strength and is suitable for use in the preparation of rocket charges when it is compression molded with nitroguanidine. The nitroguanidine additive is especially effective in reducing the impact sensitivity and lowering the temperature of combustion.

Nitroguanidine is also an explosive but it has a much lower sensitivity to impact. When 10 kg is dropped on it from a height of 100 cm, it does not explode.

Two tautomeric forms are known.



In order to obtain a solid propellant, nitroguanidine with well formed crystals, 20-100  $\mu$  long and 1.5-5  $\mu$  thick, is compression molded in amounts of 25-50% with hexogen [85].

#### Dimethyl sulphoxide

The application of dimethyl sulphoxide  $(\text{CH}_3)_2\text{SO}$  is based on its ability to form, with sodium perchlorate (and with or without water), adducts with a low melting point, which makes casting the grain much easier.

These are the adducts:  $\text{NaClO}_4 \cdot 2(\text{CH}_3)_2\text{SO}$ , mp 101-102°C and  $\text{NaClO}_4 \cdot (\text{CH}_3)_2\text{SO} \cdot \text{H}_2\text{O}$ , mp 69°C [86].

#### 6.2. Inorganic Combustible Components

These constituents, such as finely ground metals or metal hydrides, are added to propellants for the purpose of increasing the amount of energy per unit of weight and volume, which in turn increases the specific impulse.

The usefulness of the individual elements or some compounds as high energy additives is best indicated by the calorific effects (Table 6.7 and Figure 6.1) [48].

It follows from the table that beryllium and decaborane are the best of the solid substances. However, beryllium is one of the rare elements and its reserves are very limited. Moreover, its compounds are very toxic and therefore are not used.

TABLE 6.7. THE CALORIFIC EFFECTS OF HIGH-ENERGY ELEMENTS AND CHEMICAL COMPOUNDS

Substance	Formula	Density [g/ml]	(Gross) calorific value	
			kcal/kg	kcal/l
Decane	$C_{10}H_{22}$	0.729	10,573	7,700
JP-4 (hydrocarbon propellant)		0.77	10,390	8,000
Trimethyl aluminum	$Al(CH_3)_3$	0.73	10,550	7,710
Triethyl aluminum	$Al(C_2H_5)_3$	0.835	10,114	8,450
Boron	B	2.3	13,670	31,400
Beryllium	Be	1.81	15,000	27,800
Diborate (gas)	$B_2H_6$	0.44	17,800	7,712
Pentaborate (liquid)	$B_5H_9$	0.63	15,340	9,630
Decaborate (solid)	$B_{10}H_{14}$	0.92	15,310	14,100
Trimethylborine	$B(CH_3)_3$	0.62	11,500	7,400
Aluminum hydroboride	$Al(BH_4)_3$	0.558	13,750	7,670
Lithium hydroboride	$LiBH_4$	0.666	14,300	9,500
Liquid hydrogen	$H_2$	0.07	28,900	2,110
Lithium	Li	0.53	10,300	5,450
Aluminum	Al	2.7	7,290	19,700
Magnesium	Mg	1.43	6,000	8,550
Silicon	Si	2	7,160	14,350

Of course, decaborane is used, but as in the case of boron the combustion product is  $B_2O_3$ , which has a low melting point. It coats and corrodes the nozzle, thus causing considerable difficulty. The properties of the oxides of some metals are given in Table 6.8 [48]:

The most frequently used elements are: aluminum (Al), magnesium (Mg), boron

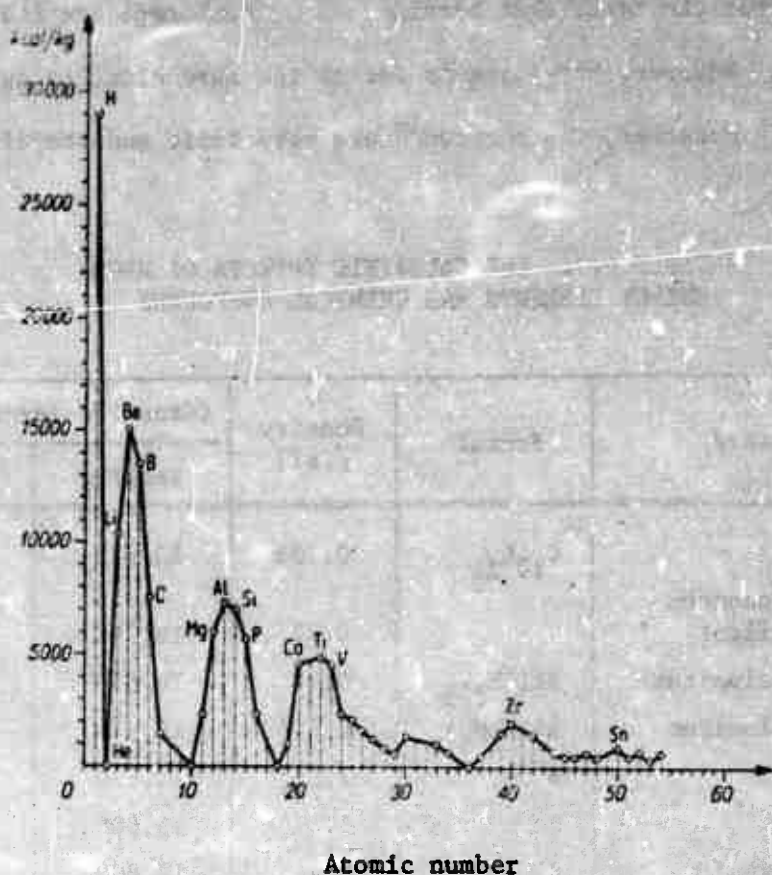


Figure 6.1. The calorific effect of chemical elements as a function of the atomic number

(B), titanium (Ti). They are relatively nonreactive. Other high-energy elements such as lithium, sodium, calcium, potassium, can be used only in exceptional cases because of their high sensitivity to moisture. The same is the case for most hydrides.

The pulverized metals are added to propellants in amounts of 2-25%, preferably 5-10%. It was learned that the addition of up to 20% aluminum increases the specific impulse by ~ 7% and also has an advantageous effect on the uniformity of combustion. Theoretical calculations indicate that the velocity of rockets or missiles can be increased 10-20% by the addition of aluminum. Propellants which usually furnish a specific impulse smaller than 250 sec can attain 260-270 seconds with boron or decaborane.

In order to assure their rapid and complete combustion, the comminution of the



TABLE 6.8. PROPERTIES OF THE HIGH-CALORIE OXIDES OF METALS

	mp [°K]	bp [°K]	Heat of fusion [kcal/mole]	Heat of vaporization [kcal/mole]
$\text{Al}_2\text{O}_3$	2320	3250 (1 ata) 3845 (20 ata)	26	115.7
$\text{B}_2\text{O}_3$	723	2520	5.5	71.8
BeO	2820	4200	17.0	
$\text{Li}_2\text{O}$	2000	2600	18.0	
MgO	3075	3350	18.5	

metals must be precise and thorough. This is particularly true in the case of boron because, during combustion, the metal particles become coated with a thin film of difficultly volatile liquid  $\text{B}_2\text{O}_3$ , which could result in incomplete combustion for the larger particles. The size of the metal particles should be of the order of 10-50  $\mu$ , preferably 20  $\mu$ , and it has also been shown that the particle shape is of prime importance. The metal dusts most frequently encountered have flat and long particles; this is not advantageous because they can form long conterminous chains which rapidly conduct heat from the combustion surface to the interior of the charge. This phenomenon is capable of causing cracks in the charge, with a resulting nonuniformity of combustion, and even rupture of the grain. The most suitable particles are those that are spherical or nearly so. In this case they make contact with each other at only one point, and this makes heat conduction difficult. However, the problem of obtaining a spherical configuration of the metal particles is a very difficult one. It has not yet been solved on a larger industrial scale because most of the present size-reduction methods are based on grinding, which tends to produce flat particles.

Metallic elements have yet another important property in addition to those

mentioned above. Their burning temperature is much higher than that of carbon and hydrogen, particularly in the case of elements with higher atomic numbers (Figure 6.2) [48].

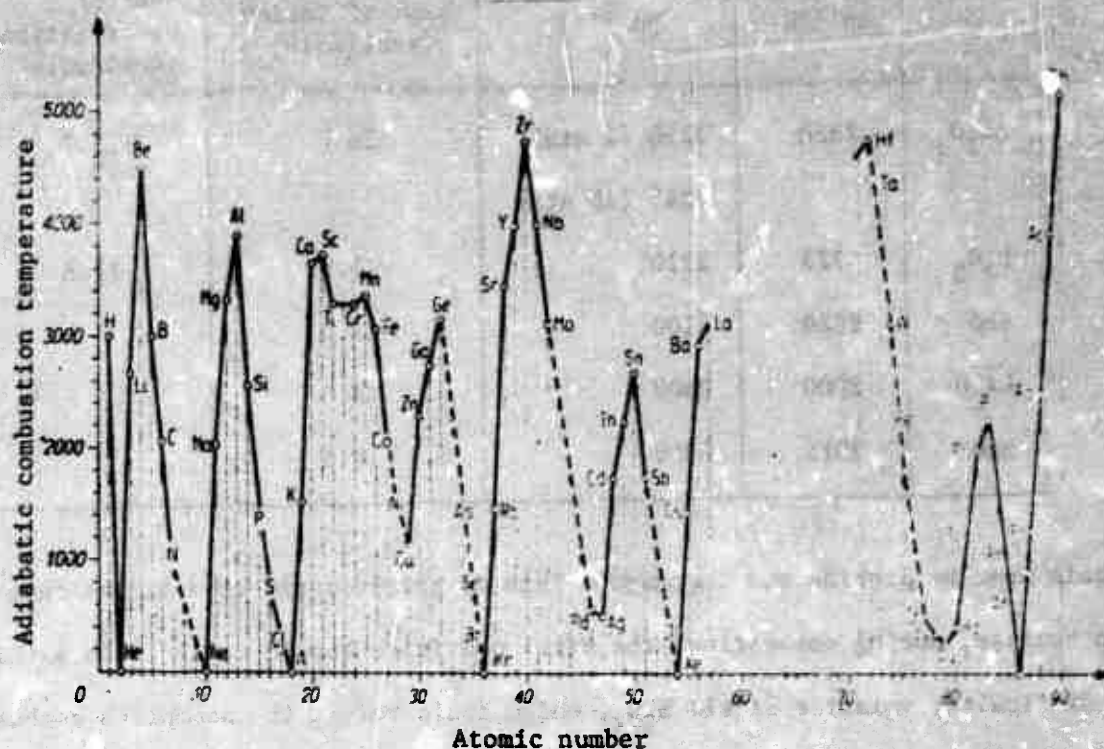


Figure 6.2. Temperature of the adiabatic combustion of chemical elements as a function of the atomic number

Due to the high combustion temperatures of these elements, such as Mg, Al and Ti, they have enjoyed wide application for so-called auxiliary charges, which are for the purpose of generating gases of high temperature and pressure so that the main charge is ignited and continues to burn uniformly (especially if the proper burning rate is not maintained under normal pressure).

In addition to the metals mentioned, hydrides are also frequently employed, particularly if they are also polymerization catalysts, e.g.,  $MgH_2$ ,  $AlH_3$ ,  $Al(BH_4)_3$ ,  $NaH$ , etc. [40, 47, 50, 56, 59, 66, 71, 75, 79, 86].

### 6.3. Plasticizers

Plasticizers are one of the most important propellant constituents. Because

liquid plasticizers are used for the most part, they facilitate mixing of the components by increasing the fluidity of the mixture. The most important characteristic, however, is their ability to improve the properties of the finished grain by increasing its elasticity or plasticity. Quite frequently, plasticizers improve the oxygen balance of the propellant if they contain oxygen atoms in the molecule, particularly in the form of nitro, nitrite or nitrate groups. Some of them even have a positive oxygen balance; thus, those that have a certain amount of active oxygen are oxidizers (e.g., nitroglycerin).

It is true that plasticizers are matched to the binder, but quite frequently the same plasticizer may be used for different binders. They constitute the following group of compounds: organic nitrates and aliphatic nitrocompounds; aromatic nitrocompounds, aromatic nitroethers, esters of polycarboxylic acids, esters of polyhydroxy alcohols and phenols, phosphoric and silicic acid esters, alcohols, glycols, polyglycols, glycol and polyglycol ethers, liquid polymers, oils, aryl-alkyl compounds, aromatic ketones, petroleum fractions, etc.

Organic nitrates are quite frequently used, particularly in colloidal fuels, as plasticizers of nitrocellulose; they are used also for other binders, but always in a mixture with non-self-oxidizing plasticizers. The organic nitrates used are, primarily: glycerin trinitrate, ethylene glycol dinitrate, diethylene glycol dinitrate, butanetriol trinitrate; n-propyl, i-propyl, n-butyl, 2-methoxy ethyl, 2-ethoxy methyl, nitro-n-propyl and nitro-n-butyl nitrates, etc.

The trinitrates and the dinitrates both have strong explosive properties. As a plasticizer of nitrocellulose, glycol dinitrate is a better solvent than nitroglycerin; consequently, it is capable of providing gels with a higher nitrocellulose content. However, glycol dinitrate has a high vapor pressure at room temperature and thus has been replaced by diethylene glycol dinitrate, which is less volatile, but nevertheless more so than nitroglycerin [6, 33, 37, 38, 51, 52, 76, 78].

Aromatic nitrocompounds. These primarily include the single-ring nitro derivatives and nitro ethers. The most important nitro derivatives are the salts of



picric and styphnic acids (2,4,6-trinitroresorcinol); these are followed by the benzene and toluene derivatives such as: nitrotoluene, nitrobenzene, 2,4-dinitrotoluene, o-dinitrobenzene, etc.; and the derivatives of diphenyl, such as o-nitrodiphenyl.

The nitrophenol ethers are of very great interest. They should contain an average of one to 3 nitro groups per benzene ring, preferably not more than 2 nitro groups per ring and not less than 2.5 groups to 2 rings.

These include 2,4-dinitrodiphenyl ether, di(dinitrophenyl)triglycol ether (resulting from the reaction of triethylene glycol with dinitrochlorobenzene), di(2,4-dinitrophenyl)propyl ether, dinitrophenylallyl ether, 2,4-dinitro anisole, 2,4-dinitro phenoxy ethanol, di(dinitro phenoxy) ethane, etc. [1, 36, 43, 49, 53, 65, 80, 81].

Polycarboxylic acid esters are the most frequently encountered plasticizers: phthalic, sebacic, adipic, citric, succinic, etc. acid derivatives, and in particular, the phthalates: dimethyl, diethyl, di(ethoxyethyl), ethyl-ethyl glycol, methyl-ethyl glycol, dibutyl, dioctyl, di(methoxyethyl), butyl-benzyl and others containing from 1 to 8 atoms of carbon in the alkyl; dibutyl, dioctyl, glycerin, etc. sebacates; dioctyl, di(3,5,5-trimethylhexyl), dibutyl adipates; trimethyl and triethyl citrates; trimethyl and triethyl acetylcitrates; and dibutyl succinate [37, 38, 39, 51, 53, 64, 67, 77, 80, 81].

Polyhydroxy alcohol esters. The most important ones here are glycol and polyglycol esters, although the esters of other alcohols are also encountered, as for example, nitromethylpropandiol diacetate or creayl-glyceryl diacetate, or the so-called acetynes, i.e., glycerin mono-, di- and triacetate.

The following glycol esters are used most frequently: diethylene glycol di-propionate, butylene glycol diacetate; triethylene glycol -- di(2-ethylbutyrate), di(2-ethylhexoate), dihexoate (Flexol 3 GH); polyethylene glycol -- di(2-ethylhexoate), dihexoate, di(2-ethylbutyrate), etc., and the glycol and polyglycol esters of the higher fatty acids [37, 38, 49, 67, 81].

The glycol polyesters and the polycarboxylic acids are plasticizers that are especially used for polyester binders, but frequently also for many other substances. Their greatest advantage lies in the fact that because they are compounds with a high molecular weight, they remain liquids with viscosities which can be adapted within broad limits, depending on the initial substrates, the degree of over-reaction and even the molecule size.

The alcohols are selected from the groups: ethylene glycol, propylene glycol, polyethylene glycol, polypropylene glycol and glycol mixtures, in which the molecular weight should be less than 200.

The polycarboxylic acids used are diglycolic acid  $(\text{HO}-\overset{\text{O}}{\parallel}\text{C}-\text{CH}_2-\text{O}-\text{CH}_2-\overset{\text{O}}{\parallel}\text{C}-\text{OH})$ ,

oxy-aceto-propionic acid  $(\text{HO}-\overset{\text{O}}{\parallel}\text{C}-\text{CH}_2-\text{O}-\text{CH}_2-\overset{\text{O}}{\parallel}\text{C}-\text{CH}_2-\text{COH})$

and oxy-dipropionic acid  $(\text{HO}-\overset{\text{O}}{\parallel}\text{C}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\overset{\text{O}}{\parallel}\text{C}-\text{CH}_2-\text{COH})$ .

1.08-1.3 moles of glycol to 1 mole of oxy-dicarboxylic acid are used in the reaction. An excess of alcohol is necessary in order to increase the degree of over-reaction. The esterification product should have a molecular weight between 250 and 1,000, preferably between 350 and 600.

The most frequently used ethylene glycol diglycolate has a specific gravity of 1.35; refraction, 1.475;  $M = 300-400$  [1, 49].

The most highly recommended aliphatic glycol ether is the plasticizer ZP-211, the fraction TP-90B of which is di(butoxy-ethoxy-ethoxy) methane with the structural formula



This compound goes under various names such as: di(butoxy-ethoxy-ethyl)

formal; di(1,4,7-trioxy-undecyl) methane or di(3,6-dioxydecyl) formal. It is a very important plasticizer for many binders [60,87].

Phosphoric acid esters are universally known plasticizers. They are: tricresyl, triphenyl, ethyl-diphenyl, tributyl, and octyl-diphenyl phosphates. The plasticizer Cellosolve with formula  $OP(OCH_2CH_2-O-C_4H_9)_3$  is also a representative of this group [38, 50, 77, 87].

Sulfonamides. Plasticizers of this type are suitable for only a few binders. Thus, for example, the plasticizers, N-ethyl-o-toluene sulfonamide or N-ethyl-p-toluene sulfonamide, can be used with the cellulose esters or the polylactams [38, 75].

The group of hydrocarbons, oils, petroleum derivatives and others includes: the plasticizers, Pentaryl A -- monoamyl-diphenyl; Paraflux -- a mixture of saturated hydrocarbon polymers; Circosol-2XH -- petroleum hydrocarbons with a sp. gr. of 0.94 and Saybolt viscosity of about 2,000 seconds at 37.8°C; and castor oil (most frequently, a softener of asphalts) and benzophenone [3, 40, 58, 61, 63, 64, 71].

The alcohol group contains nonvolatile liquid aliphatic alcohols of the glycol type, such as ethylene, di-, tri- and polyethylene glycols, polypropylene glycols, etc.; aromatic-aliphatic alcohols as, for example, benzyl alcohol (a good plasticizer of polyester-styrene resins) [39, 59, 67, 69].

Plasticizers are added to binders in quite different amounts, depending on the softener, the binder and propellant constituents as well as on the desired propellant properties. Nevertheless, the plasticizers should be more than 25% by volume, preferably 50%, but not more than 82% of the combustible component.



## 7. OTHER SOLID PROPELLANT CONSTITUENTS

In addition to the oxidizer, the combustible component and the inorganic combustible substance, other constituents are present in propellants in much smaller quantities but are by no means less important. Some of these, such as vulcanizers or polymerization catalyzers, do not require a great deal of discussion because they are substances that are already universally known in the field of polymer or natural rubber chemistry. Other additives are specific for solid propellants, however, and will be discussed more thoroughly.

### 7.1. Stabilizers

Stabilizers are substances that counteract ageing of the propellant and thus extend the time of usefulness, reckoned from the time of manufacture of the grain. Stabilizers are different types of compounds which act in different manners, matched to the mechanism of ageing of the given propellant. After all, there are a great many factors that affect the ageing; frequently, several of them at the same time.

Ageing is defined as changes in the physical and chemical properties caused by depolymerization effects, breaking of the binder chains, binder crystallization, phase changes, oxidizer activity, etc., whereby the following phenomena are manifested: an increase in the fraction dissolved in the corresponding solvents (the fraction being extracted from the binder), and a decrease in the number of transverse bonds (measured by the swelling method). Chain decay is caused by oxidation, reduction, hydrolysis, etc.

A certain amount of volatile compounds results from the decomposition reaction; this leads to an increased porosity. The rate of crystallization is greatest just below the melting point; thus, it is necessary to avoid keeping the propellant at these temperatures for a prolonged period of time. The oxidizer causes ageing by reacting with the combustible component at the interface and by reaction of the oxidizer fraction dissolved in the combustible component. Moreover, it has been shown

that hardening or polymerization catalyzers can have an influence on binder decomposition (e.g., organic peroxides decompose rubber).

In order to counteract ageing, thermally and chemically stable binders should be chosen, weak bonds should be avoided, groups with a high resonance energy are to be desired, readily crystallizing substances must be avoided, polymerization or hardening catalyzers should be used in small amounts or not at all, inert (neutral) oxidizers must be used and, finally, stabilizers must be used.

Stabilizers act in different ways, some chemically and others physically. The chemical method is based on the binding of the propellant decomposition products, which would be autocatalyzers of further decomposition. Another group of stabilizers includes anti-oxidizers which counteract binder oxidation by reacting with the oxidizing agents (these undergo oxidation themselves).

Stabilizers with a physical action are primarily surface-active substances and will for the most part be discussed with that group of compounds from the viewpoint of their other properties, which are more important than their stabilizing activity. It is necessary only to mention the mechanism of their action. Upon being adsorbed on the oxidizer-combustible component interface, surface-active substances form a layer which separates these 2 substances, thus making an oxidation reaction impossible.

A measure of the stability of rocket propellants is the gassing test. The quantity (by volume) of gaseous products liberated from 1 g of propellant at 135°C when heated for one, 2 and 3 hours is determined [80]. If  $\sim 2 \text{ cm}^3$  of gases per gram of substance are evolved after the first hour, the propellant should be stable for 30 days at 77°C. Stabilizers called gassing inhibitors are added to reduce gassing [49,80].

Stabilizer research began with the discovery of nitrocellulose powders. The reason for this was the problem which arose concerning the binding of acid decomposition products, which had a catalytic action on further decomposition, frequently leading to self-ignition or explosion. Both inorganic and organic substances were

used in this case and some of them are still being used.

#### 7.1.1. Inorganic stabilizers

Inorganic stabilizers are primarily carbonic acid salts. This is understandable because propellant decomposition products have an acid nature and when gaseous  $\text{CO}_2$  is liberated, salts are formed which do not corrode the grain. Thus, the following are used: sodium, calcium, magnesium and ammonium carbonates, as well as sodium acid carbonate. It is rarely possible to employ sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) without undesirable results because its high alkalinity can cause binder decomposition; it is not suitable for nitrocellulose powders. Sodium acid carbonate does not have such an alkaline reaction, which makes it better than dibasic sodium carbonate. Being difficultly soluble, calcium and magnesium carbonates do not exhibit an alkaline reaction and can be successfully used even for readily soluble binders; however, they have a stabilizing action only in larger amounts. Such increases in inorganic substance contents have an adverse effect in that they reduce the specific impulse. Moreover, all carbonates have one drawback in that they evolve gaseous  $\text{CO}_2$  when reacting with the acid decomposition products of the propellant and this in turn increases the porosity of the grain [33, 64, 76].

Magnesium oxide ( $\text{MgO}$ ) is an inorganic stabilizer which eliminates the above inconvenience. It is a propellant constituent which is very often used because it is also capable of increasing the burning rate and counteracting the production of smoke. It is present in propellants in amounts of 0.2-0.5% and it is added in 0-5 parts by weight to 100 parts by weight of resin [36, 59, 61, 63].

#### 7.1.2. Organic stabilizers

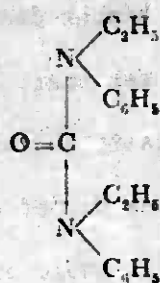
These stabilizers are universally used and basically they form 2 groups of compounds: inorganic salts of weak organic acids and amines or amides.

The salts of weak organic acids have an action similar to that of the inorganic carbonates in that the organic acid evolved is a liquid or a solid. Thus, e.g., a propellant containing polyvinyl chloride evolves a certain amount of hydrogen

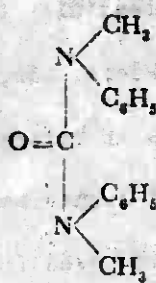


chloride (HCl), which has a corrosive action on the grain, when it hardens at an elevated temperature. The addition of 0.5-1% of barium castorate completely prevents corrosion [37].

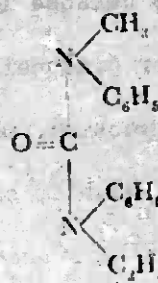
Compounds of the amide-urea derivative type are familiar stabilizers and they are good, particularly Centralite I (sym-diphenyl-diethyl urea) and Centralite II (sym-diphenyl-dimethyl urea) and the mixed Centralite (N-ethyl-phenyl-N'-methyl-phenyl urea) as well as Acardite (asym-diphenyl urea).



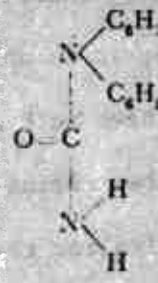
Centralite I



Centralite II



Mixed Centralite



Acardite

They are used for colloidal fuels. They exert a stabilizing effect by forming compounds with the nitrogen oxides arising in the propellant during the ageing process. Namely, the aromatic rings undergo nitration; also the bonds between the nitrogen atom and the  $-\text{CO}-$  group often break and nitrosoamines are formed. The Centralites and Acardite are most frequently employed in amounts of 1% in relation to the entire propellant [6, 76, 77, 78].

Quite frequently, the stabilizer anti-oxidizer is Flexamine. This is a mixture of 65% diarylamine complex with ketone and 35% N,N'-diphenyl-p-phenylene diamine



This mixture is used in amounts of 3-5% in relation to the resin; in relation to the entire combustible component,  $\sim 2\%$ ; and in relation to the propellant,  $\sim 0.3\%$ , whereby yet another stabilizer is frequently added (e.g., phenyl- $\beta$ -naphthylamine).

The stabilizers-gassing inhibitors are aromatic or alkyl-aromatic amines with

the formula  $RZ(NR'R'')_x$ ; where  $z$  = an aromatic phenyl or naphthyl ring;  $R$  = H or alkyls with 1-12 C;  $R'$  and  $R''$  = H or alkyls with 1-4 C; and  $x$  = 1-3.

In particular, they are:

aniline	diphenyl amine
dinaphthylamine ( $\alpha$ or $\beta$ )	phenyl naphthylamine ( $\alpha$ or $\beta$ )
1-naphthylamine	toluidine
xylydine	p-dodecyl aniline
N-methyl aniline	N,N-dimethyl aniline
N-sec-butyl aniline	dodecyl diamino naphthalene
diaminobenzene	N-sec-butyl diamine benzene
diaminonaphthalene	N-methyl diaminonaphthalene
methyl diaminonaphthalene	triaminobenzene
triaminonaphthalene	triaminotoluene
triaminomethyl naphthalene	

These amines are used in quantities of less than 10% of the binder; in relation to the entire propellant, between 0.5% and 4%.

The effectiveness of action of some amines as inhibitors of gassing for a propellant with the composition

	%
ammonium nitrate ( $NH_4NO_3$ )	73.00
insoluble Prussian blue	3.00
Norit A (a type of carbon black)	0.80
carbon black	0.20
cellulose acetate	4.76
ethylene glycol diglycolate	7.97
2,4-dinitro diphenyl ether	7.97
acetonylacetone dioxime	2.30

is given in Table 7.1 with a 2% amine content instead of dioxime.

It is evident from the above that N-alkyl derivatives of aniline, 2,4-diaminotoluene and N,N-dimethyl-p-toluidine have the best stabilizing properties. It was also learned that carbon black and Prussian blue cause an increase in gassing.

TABLE 7.1. THE INFLUENCE OF GASSING INHIBITORS

Inhibitor	Gassing rate in cm <sup>3</sup> /g/hour		
	1 hour	2 hours	3 hours
Standard	21	6.4	5.8
Diphenylamine	8.8	4.2	-
Diphenylamine with a propellant without carbon black	0.5	1.8	4.0
Phenyl- $\beta$ -naphthylamine	0.0	1.0	1.7
N,N-methyl-ethylaniline	0.0	0.0	1.1
Aniline	0.6	0.0	5.8
N-methyl aniline	0.6	0.3	0.3
N,N-dimethyl aniline	0.0	0.0	1.5
2,4-diaminotoluene	0.0	0.0	0.6
N,N-dimethyl-p-toluidine	0.0	0.0	7.0
p-phenylene diamine	1.3	0.4	2.5
o-phenylene diamine	1.3	0.4	3.5
p-dodecyl aniline	4.0	-	-

Diphenyl amine is a stabilizer that has been widely used formerly and is still widely used today. However, it does not furnish satisfactory results in the presence of carbon black and oximes. On the other hand, a propellant of composition:

	%
NH <sub>4</sub> NO <sub>3</sub>	74.00
cellulose acetate	8.05
ethylene glycol diglycolate	5.75
2,4-dinitro-diphenyl ether	9.2
Prussian blue	3.0

thus without carbon black and oxime, exhibits a gassing of 2 cm<sup>3</sup>/g after the first hour; after the addition of 2% diphenylamine, the gassing amounts to only 0.5 cm<sup>3</sup>/g/hour, which is entirely satisfactory.



The influence of Prussian blue is even more strongly marked. A propellant in which 2/3 of the Prussian blue was replaced by another combustion catalyzer, namely, ammonium dichromate  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ , was studied. The composition of the propellant was then as follows:

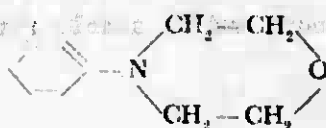
	%
$\text{NH}_4\text{NO}_3$	73.00
insoluble Prussian blue	1.00
$(\text{NH}_4)_2\text{Cr}_2\text{O}_7$	2.00
Norit A (a type of carbon black)	0.80
carbon black	0.20
cellulose acetate	4.76
ethylene glycol diglycolate	7.97
2,4-dinitro-diphenyl ether	7.97
acetonylacetone dioxime	2.30

This propellant does not produce gas during the first hour. During the second hour,  $1 \text{ cm}^3/\text{g}$  of gas evolves and after 3 hours, the evolution is  $3.7 \text{ cm}^3/\text{g}/\text{hour}$ .

Following addition of 2% diphenylamine, the mixture does not produce gas until after 6.5 hours and scarcely  $1.9 \text{ cm}^3$  of gas is evolved after  $7 \frac{3}{4}$  hours.

In selecting appropriate amines, close attention must also be given to their alkalinity. Thus, e.g., aniline cannot be used as a stabilizer of colloidal fuels because of its relatively high basicity [49,80].

N-phenyl morpholine



in a ratio of 5:1 can be added to the aromatic amines to improve stabilization [113].

### 7.1.3. The stabilizing action of surface-active agents

As already mentioned, surface-active agents extend the useful life of propellants. For example,

Propellant 1.

	%
cellulose acetate	6.75
2,4-dinitro-diphenyl ether	7.88
ethylene glycol diglycolate	5.85
diphenylamine	2.02
Arlacel C (a surface-active compound -- one of the sorbitan oleates)	0.10
$\text{NH}_4\text{NO}_3$	73.9
carbon black	0.5
insoluble Prussian blue	1.0
$(\text{NH}_4)_2\text{Cr}_2\text{O}_7$	2.0

does not produce gas for 2 hours and is stable for 80 days at a temperature of 77°C.

Propellant 2. A similar propellant without a surface-active agent and having the following composition:

	%
cellulose acetate	6.9
2,4-dinitro-diphenyl ether	8.05
ethylene glycol diglycolate	5.98
diphenylamine	2.07
Prussian blue	1.00
$(\text{NH}_4)_2\text{Cr}_2\text{O}_7$	2.00
carbon black	0.50
$\text{NH}_4\text{NO}_3$	73.50

does not produce gas for 1.5 hours and is stable for only 7 days at 77°C.

Propellant 3.

	%
cellulose acetate	6.57
2,4-dinitro-diphenyl ether	7.66
ethylene glycol diglycolate	5.70
diphenylamine	1.97
insoluble Prussian blue	1.00
$(\text{NH}_4)_2\text{Cr}_2\text{O}_7$	2.00

	2
carbon black	2.00
Span 85 (a surface-active compound of the sorbitan oleate group (Sorbitan trioleate))	0.10
$\text{NH}_4\text{NO}_3$	73.00

is stable for 30 days at 77°C.

Propellant 4 with a composition like that of propellant 2 with the addition of 0.1% Nonisol-250 or 0.1% Pluronic L-62 (an ethylene polycyde monoester and an ethylene oxide copolymer with propylene oxide, respectively) is stable for 30 days at 77°C.

It is evident from the above that the addition of 0.1% of a surface-active agent is capable of extending the "life" of the propellant by 4 or more times [43].

## 7.2. Substances that Influence the Burning Rate r

These are combustion "catalyzers", moderators, combustion modifiers and the substances that influence the burning rate indirectly.

### 7.2.1. Combustion "catalyzers"

As already discussed in detail, the mechanisms of action of combustion "catalyzers" are quite divergent and frequently composite. It is not yet always possible to determine the mechanism of action of a specific "catalyzer", nor is it always possible to determine the predominant mechanism of action. Furthermore, the term, combustion "catalyzer", is not a very precise definition and it is retained only because of its universal usage.

Strictly speaking, the term, combustion "catalyzer", should be applied only to those substances which are added to the propellant for the sole purpose of increasing the burning rate. The limitation imposed by the word "sole" signifies that many substances added to propellants for another purpose have a secondary action similar to or the same as the combustion "catalyzers" but belong to other constituent groups



because of their principal applications.

Substances that increase the burning rate can be organic or inorganic compounds as well as elements. Organic compounds exert an action here by absorbing high-energy radiation, by decomposing exothermically and producing chemiluminescent  $C_2^*$  molecules, etc. If these are organic salts of metals, chemiluminescence of the metals can also be expected (if, of course, the metal possesses a high-energy excitation state).

Inorganic compounds have a similar mechanism of action. On the other hand, metallic elements exert their influence either through chemiluminescence or by an exothermic reaction with the oxidizer.

#### Chromates

Chromates, dichromates, trichromates and tetrachromates are widely used as combustion "catalyzers". Chromium itself does not exhibit chemiluminescence and is not effective; thus, it is not used. On the other hand, the chromates and polychromates undergo exothermic decomposition, and they possess the well known property of absorbing high-energy radiation. To this can be added the chemiluminescence of excited potassium or lead atoms if  $K_2Cr_2O_7$  or  $PbCrO_4$  are used.

Ammonium dichromate has proved to be the best of this group. It has the highest heat of decomposition due to intramolecular oxidation of the  $NH_4^+$  groups



It is added to the propellant after mixing with the oxidizer. The comminution should be of the order of 0.02-40  $\mu$  particle size, most preferably  $\sim 15 \mu$ . The amounts used range from 3 to 10% of the propellant. However, it is better to hold to the lower limit. Ammonium dichromate can also be used in mixtures with other "catalyzers", but then it is used in smaller quantities.

In addition to the above, ammonium chromate,  $(NH_4)_2CrO_4$ ; sodium chromate,  $Na_2CrO_4$ ; potassium chromate,  $K_2CrO_4$ ; and sodium dichromate,  $Na_2Cr_2O_7$  are used.

Among the organic salts, aliphatic and cyclo-aliphatic amine chromates, e.g., ethylene diamine or dimethyl piperazine chromates, have proved to be effective. The organic chromates are used in amounts up to 4% of the propellant [36, 39, 43, 44, 49, 61, 62, 63, 65, 67, 80, 81].

Among the polychromates, ammonium trichromate  $(\text{NH}_4)_2\text{Cr}_3\text{O}_{10}$  and ammonium tetrachromate  $(\text{NH}_4)_2\text{Cr}_4\text{O}_{13}$  in amounts up to 1% of the propellant act to increase the burning rate by about 45%, to reduce the temperature coefficient of the burning rate at constant pressure  $\bar{u}$  by about 15-40% and to reduce the temperature coefficient of pressure  $\pi_p$  by about 30-40%.

This effect on a propellant of composition:

	%
$\text{NH}_4\text{ClO}_4$	75.00
polyester	12.35
ethylene glycol	47.00%
adipic acid	49.45%
maleic anhydride	3.55%
styrene	12.35
cumene hydrogen peroxide	0.25
lecithin	0.05
	100.00

(hardened at 104°C) at a temperature of 15.6°C and at a pressure of 70.3 kg/cm<sup>2</sup> is given in Table 7.2.

Tri- and tetrachromates are used in amounts of 0.10-4.0% of the propellant. Their decomposition temperature is higher than 238°C [5,80].

As in the case of the chromates, ammonium molybdate  $(\text{NH}_4)_2\text{MoO}_4$  exerts its action through exothermic decomposition; however, it is rarely used [60]. Among the other chromium compounds, we have  $\text{Cr}(\text{NO}_3)_3$ , which is also rarely used; on the other hand, chromium oxide,  $\text{Cr}_2\text{O}_3$ , merits greater discussion.

TABLE 7.2. THE INFLUENCE OF  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  ON THE BURNING RATE AND ON THE COEFFICIENTS  $u$ ,  $\pi_p$  AND  $n$

	Burning rate $r$ [cm/sec]	$u$ [%/1°C]	$\pi_p$ [%/1°C]	$n$
Standard I	0.693	0.25	0.45	0.42
Standard +1% $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$	1.003	0.16	0.27	0.40
Standard II	0.688	0.27	0.56	0.51
+0.10% $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$	0.864	0.22	0.38	0.45
+0.25% $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$	0.930	0.23	0.38	0.41
+0.50% $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$	0.915	0.29	0.54	0.44
+1.00% $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$	0.947	0.23	0.40	0.40

#### Metal oxides

Chromium oxide,  $\text{Cr}_2\text{O}_3$ , is a stable compound and reacts only by absorbing radiation. This effect can be significantly increased by various additives. Therefore,  $\text{Cr}_2\text{O}_3$  most frequently appears with other oxides, which are primarily derivatives of metals capable of chemiluminescence. These are  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{TiO}_2$ ,  $\text{SnO}_2$ ,  $\text{CuO}$ ,  $\text{PbO}$ ,  $\text{Pb}_2\text{O}_3$  and  $\text{ZnO}$ ,  $\text{Al}_2\text{O}_3$ , etc. These oxides are added to chromium oxide in amounts from traces to 50%. A mixture of  $\text{Cr}_2\text{O}_3$  with aluminum silicate (acid-activated), available under the name "Filtrol", is also effective. The above "catalyzers" are used in amounts of 1-4%. With a 1% content the increase in the burning rate is about 0.3 cm/sec [36, 59, 80, 82].

Some oxides, such as  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{Pb}_2\text{O}_3$ ,  $\text{PbO}$  and  $\text{CuO}$ , can be used independently in amounts ranging from 0.2-7% and with a comminution to about 15  $\mu$  particle size [61, 76, 77].



## Chromites

Cupric chromite  $\text{CuO} \cdot \text{Cr}_2\text{O}_3$  has been shown to be one of the most effective combustion "catalyzers" [36, 39, 58, 67, 80, 88].

Other chromites are less effective; nevertheless, they are also sometimes used. The activity of cupric chromite is a function of its purity. The impure chromite with incompletely reacted  $\text{CuO}$  and  $\text{Cr}_2\text{O}_3$  is more effective than the pure compound. However, these differences are not great, because cupric chromite is very active in all forms. This activity is also a function of the particle size, as indicated in Table 7.3 for propellants based on  $\text{NH}_4\text{ClO}_4$  (or  $\text{KClO}_4$ ) and with a combustible component composed of polyvinyl chloride and dibutyl sebacate in a ratio of 1:1. Some of the above data are given in Figure 7.1.

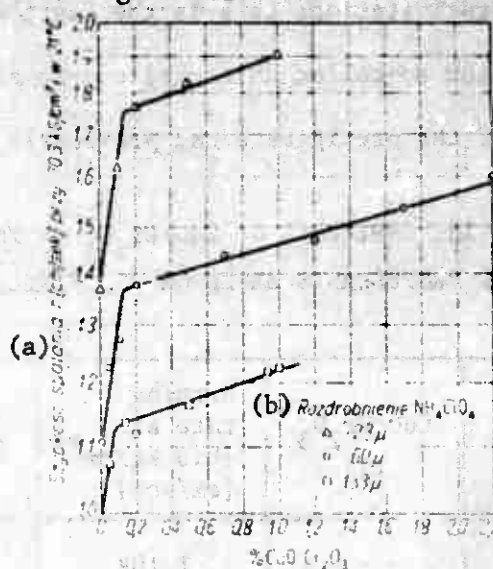


Figure 7.1. The influence of oxidizer size-reduction on the effectiveness of  $\text{CuO} \cdot \text{Cr}_2\text{O}_3$ .

Key: (a) = burning rate  $r$  (cm/sec) at 70.3  $\text{kg/cm}^2$  and at 21°C and (b) = particle size of  $\text{NH}_4\text{ClO}_4$ .

It follows from this that the greatest increase in the burning rate is observed with  $\text{CuO} \cdot \text{Cr}_2\text{O}_3$  contents of 0.1-0.15%. A lowering of the particle size of the oxidizer from 133  $\mu$  to 60  $\mu$  causes an increase in the burning rate of 14%, and a lowering to 23  $\mu$  results in an increase of 42%; at the same time, a decrease in the particle size of the oxidizer leads to an increase in the effectiveness of  $\text{CuO} \cdot \text{Cr}_2\text{O}_3$ . Thus,

a 1% addition of chromite in the case of particle sizes of 133  $\mu$  increases the burning rate by 29%; with particle sizes of 60  $\mu$ , by 32%; and with 23  $\mu$ , by 39%. However, this same chromite (by itself) has no effect or may even lower the burning rate in propellants based on potassium perchlorate ( $\text{KClO}_4$ ).

In Table 7.4, we present the data on other chromites as compared with  $\text{CuO} \cdot \text{Cr}_2\text{O}_3$  in propellants with a composition of  $\text{NH}_4\text{ClO}_4$ , polyester and styrene 1:1 and with an oxidizer particle size of 60  $\mu$ . It is immediately evident that no other chromite exceeds the effectiveness of cupric chromite.

The above chromites are obtained in the following manner: 72.6 g of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  are dissolved in 240 ml of water. This is heated to 70°C, and a solution of 37.8 g of  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  in 180 ml of water with 45 ml of 28% aq.  $\text{NH}_3$  is added to it. After mixing, there is a precipitation; this is the inert ammoniocupric chromate, which is dried at 110°C. The so-called unleached cupric chromite appears after roasting in a crucible. If the precipitate had previously been washed twice

TABLE 7.3. THE INFLUENCE OF  $\text{CuO} \cdot \text{Cr}_2\text{O}_3$  ON THE BURNING RATE OF SOME PROPELLANTS BASED ON POLYVINYL CHLORIDE

Oxidizer [%]	Mean particle size [ $\mu$ ]	$\text{CuO} \cdot \text{Cr}_2\text{O}_3$ [%]	Burning rate at 70.3 kg/cm <sup>2</sup> [cm/sec]	Increase in r [%]	$\bar{n}$ at 70.3 kg/cm <sup>2</sup>
$\text{NH}_4\text{ClO}_4$ 75	60	-	1.102	-	0.42
		0.05	1.232	12	0.41
		0.10	1.283	16	0.37
		0.20	1.377	25	0.37
		0.50	1.407	28	0.37
		1.00	1.455	32	0.36
		1.50	1.526	38	0.38
		2.00	1.600	45	0.38
		3.00	1.557	41	0.36
77.5	60	-	1.219	-	0.43
		1.00	1.575	29	0.36
80	60	-	1.321	-	0.47

TABLE 7.3. (continued)

Oxidizer [%]	Mean particle size [ $\mu$ ]	$\text{CuO} \cdot \text{Cr}_2\text{O}_3$ [%]	Burning rate at 70.3 kg/cm <sup>2</sup> [cm/sec]	Increase in $\underline{r}$ [%]	$\underline{n}$ at 70.3 kg/cm <sup>2</sup>
75.0	23	0.05	1.473	12	0.41
		0.08	1.499	13	0.41
		0.14	1.549	17	0.39
		0.20	1.600	21	0.39
		0.60	1.600	33	0.37
		1.00	1.778	35	0.38
		-	1.372	-	0.48
		0.10	1.628	19	0.38
		0.20	1.758	28	0.38
		0.50	1.831	34	0.38
75.0	133	1.00	1.900	39	0.41
		-	0.965	-	0.45
		0.02	0.983	2	0.39
		0.05	1.073	11	0.40
		0.14	1.138	18	0.37
		0.20	1.112	15	0.39
		0.50	1.168	21	0.38
		0.95	1.214	26	0.38
		1.00	1.250	29	0.38
		-	0.800	-	0.60
70.0	60	0.10	0.965	17	0.32
60.0	60	-	0.541	-	0.64
		0.10	0.678	25	0.21
		1.00	0.838	55	0.37
60.0	60	-	0.325	-	0.64
		0.10	0.419	29	0.31
		1.00	0.565	73	0.41
KC10 <sub>4</sub> 80	ground in a micromill (6900 rpm)	-	2.485	-	0.70
		0.10	2.485	0	0.69
		0.50	2.485	0	0.63
70		-	1.778	-	0.85
		0.50	1.676	6	0.76



with dilute acetic acid, the so-called leached chromite,  $\text{CuO}:\text{Cr}_2\text{O}_3 = 1:1$ , would have been obtained after drying and roasting.

The cupric chromite  $\text{CuO}:\text{Cr}_2\text{O}_3 = 84:15.3$  is obtained by roasting the precipitate which appears when solutions of 127 g of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in water and 12.8 g of  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  are mixed and aq.  $\text{NH}_3$  is neutralized.

TABLE 7.4. THE EFFECT OF VARIOUS CHROMATES AND CHROMITES ON THE BURNING RATE OF SOME PROPELLANTS WITH POLYESTER-STYRENE BINDERS

Catalyzer	%	Burning rate $\bar{r}$ at 70.3 $\text{kg/cm}^2$ [cm/sec]	Increase in $\bar{r}$ [%]	$\bar{n}$ at 70.3 $\text{kg/cm}^2$
-	-	1.103	-	0.42
Ammoniocupric chromate	1	1.354	23	0.402
Leached $\text{CuO} \cdot \text{Cr}_2\text{O}_3$ (1:1)	1	1.387	26	0.381
Unleached $\text{CuO} \cdot \text{Cr}_2\text{O}_3$	1	1.443	31	0.371
Cupric-cadmium-zinc chromite	1	1.331	21	0.415
$\text{CuO} \cdot \text{Cr}_2\text{O}_3$ (84:15.3)	1	1.484	35	0.352
Cupric-magnesium chromite	1	1.417	29	0.324
Ferric chromite	0.25	1.255	14	0.39
Ammonio-cupric-cadmium-zinc chromate	1	1.293	17	0.42

Cupric-cadmium-zinc chromite is obtained by roasting the precipitate occurring from the mixing of solutions of 4.6 g of  $\text{Cd}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , 4.8 g of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and 47.4 g of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  in 100 ml of water and 25.2 g of  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  in 100 ml of water and then neutralizing with 15 ml of a 28% ammonia solution.

Magnesium-cupric chromite is obtained by roasting the precipitate resulting from the mixing of solutions of 63 g of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and 32 g of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  with 3.2 g of  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  and then neutralizing with aqueous  $\text{NH}_3$ .

Due to the good solubility of ferric chromite, it is obtained in a somewhat

different manner. 67.33 g of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  is dissolved in 500 ml of water and the hydroxide is precipitated with ammonia. Then, an aqueous solution of 50 g of  $\text{CrO}_3$  is added. The chromate crystallizes during evaporation; the product obtained is subjected to roasting [89].

#### Perchlorates

The perchlorates of such metals as chromium (Cr), cobalt (Co), iron (Fe), manganese (Mn), silver (Ag) and copper (Cu) have proved to be very active catalyzers.

Some of them increase the burning rate by more than 100% (ferric perchlorate).

The activity of the above perchlorates is given in Table 7.5 [90] for a propellant of composition:

	%
$(\text{NH}_4)_2\text{Cr}_2\text{O}_7$	1.99
$\text{NH}_4\text{NO}_3$	72.79
polyester	9.79
diethylene glycol	43.00 parts by weight
adipic acid	44.25 " " "
maleic anhydride	1.75 " " "
styrene	2.66
methyl acrylate	12.28
polymerization catalyzer + lecithin	0.49
	100.00

TABLE 7.5. THE EFFECT OF THE PERCHLORATES OF VARIOUS METALS ON THE BURNING RATE OF A PROPELLANT WITH A BINDER CONTAINING POLYESTERS, STYRENE AND METHYL ACRYLATE

Perchlorates	%	Burning rate $\bar{r}$ at 70.3 kg/cm <sup>2</sup> [cm/sec]
-	-	0.178
Chromium (Cr) (ic)	1	0.305
Cobalt (Co)	1	0.330
Ferric (Fe)	1	0.381
Manganic (Mn)	1	0.330
Silver (Ag)	1	0.305
Cupric (Cu)	1	0.279

## Silicates and titanates

Organic silicates: methyl, ethyl, propyl, i-propyl; titanates: methyl, ethyl; some inorganic silicates such as calcium silicate; and earths treated with amines have the ability of increasing the burning rates of propellants based on ammonium oxidizers by 100% and even more. In this case they exhibit a synergic action with ammonium dichromate  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ . The best "catalyzer" is one with a composition of 1-50%  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  and 50-99% silicates or titanates.

By way of example, the influence of ethyl silicate on a propellant of composition:

$\text{NH}_4\text{ClO}_4$		%
polyester		85.00
		3.58
ethylene glycol	43 parts by weight	
adipic acid	44.25 " " "	
maleic anhydride	1.75 " " "	
n-butyl acrylate		9.33
methyl acrylate		1.44
methylethyl ketone peroxide		0.40
lecithin		0.25
		100.00

is presented in Table 7.6

TABLE 7.6. THE EFFECT OF ETHYL SILICATE ON THE BURNING RATE OF A PROPELLANT WITH A BINDER CONTAINING POLYESTERS AND ACRYLATES

Catalyzer	%	Burning rate $\bar{r}$ at 70.3 kg/cm <sup>2</sup> and at 15.6°C [cm/sec]	$\Delta r$ [%]
-	-	1.016	-
Ethyl silicate	1	2.184	115
$(\text{NH}_4)_2\text{Cr}_2\text{O}_7^*$	1	1.270	25
Ethyl silicate 2/3	1.5	2.438	140
$(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ 1/3			



\*(See Table 7.6) The data for  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  are correct for a somewhat different propellant composition but, because of the slight difference, they can also be assumed for the above composition.

It follows from this Table that the addition of 1.5% of the mixed "catalyzer" has the same effect as the combined effect of 1%  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  and 1% ethyl silicate [91].

#### Lead salts

Because lead is an element with a high chemiluminescence, it induces an increase in the burning rate both as a metal and in the form of salts. In this respect, one of its best compounds is plumbous chloride ( $\text{PbCl}_2$ ). When added in the amounts of 0.05-5% to propellants based on ammonium oxidizers, it increases the burning rate by almost 100%. In the case of these propellants, it is more often used together with ammonium dichromate  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ .

For example, for propellants of compositions:

	A	B
	%	%
$(\text{NH}_4)_2\text{Cr}_2\text{O}_7$	1.99	2.00
$\text{NH}_4\text{NO}_3$	72.79	76.00
polyester	9.79	5.82
diethylene glycol	43 parts by weight	47.00%
adipic acid	44.25 " " "	49.45%
maleic anhydride	1.75 " " "	3.55%
styrene	2.66	2.79
methyl acrylate	12.28	12.49
polymerization catalyzer + lecithin	0.94	0.80
cobalt octanoate	-	0.10
	100.00	100.00

The effect of  $\text{PbCl}_2$  is as follows:

Propellant	PbCl <sub>2</sub> %	Burning rate at 70.3 kg/cm <sup>2</sup> cm/sec
A	-	0.178
A	1	0.330
B	-	does not burn
B	0.5	0.279

The lead (plumbous) chloride is ground and added to the binder at the same time as the oxidizer [92].

Other lead salts used as "catalyzers" are lead sulfide (PbS), lead azide (PbN<sub>6</sub>) and lead stearate [76, 78, 92].

#### Metallic elements

Metallic elements such as powdered copper (Cu) in amounts of 0.5-7% and with a particle size of 15  $\mu$ , powdered iron and aluminum are also capable of increasing the burning rate. Titanium in amounts greater than 2% increases the burning rate, and at the same time it is a good inorganic combustible component [36, 50, 59, 76, 78].

In addition, metallic soaps, e.g., aluminum stearate in an amount of about 2%, facilitate the oxidation of metallic combustible components such as aluminum (Al), magnesium (Mg), etc. [79].

#### The Prussian blue group

A group of combustion "catalyzers" universally used today consists of substances analogous to Prussian blue, that is, derivatives of ferri- and ferro-cyanides. There are a great number of them and they are of divergent effectiveness. They are Prussian, steel, bronze, Milori, Turnbull, Chinese, new, Antwerp, mineral, Berlin, Hamburg, water, Williamson, Erlanger, Paris and other blues. Milori and Prussian blues are the ones most frequently encountered.

Milori blue is the oxidation product of potassium ferrocyanide  $K_4Fe(CN)_6$  paste and ferrous sulfate  $FeSO_4$  in the presence of small amounts of naphthenic acids. An electron microgram, enlarged 50,000 times, shows that the particles are of uniform

size, are almost spherical and form short chains. If naphthenic acids are not used, the particles are more crystalline, agglomerated and much larger. Because it is difficult to remove the water from the paste obtained in the usual manner, the best method is to mix it with the plasticizer and treat it with a surface-active agent capable of driving the water out of the "catalyzer" surface, thus facilitating its removal during drying. Ethomeens, an ethylene oxide substituted with alkylamines, is such a surface-active agent. Naphthenic acids are added to Milori blue in amounts of 1.5-2.5%.

Prussian blues are of 2 types: soluble and insoluble in water. The insoluble type is represented by ferric ferro-cyanide  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ ; while the soluble ferro-cyanides are: iron-potassium (ic), iron-sodium (ic), iron-ammonium (ic) and iron-ammonium-sodium (ic).

The insoluble blues are most effective, but propellants containing them in amounts less than 6% are difficult to ignite, although they are readily ignited under an increased pressure. On the other hand, soluble Prussian blues facilitate ignition under normal pressure.

Another type of Prussian blue is known: ammonia Prussian blue. It has the "catalytic" property of insoluble Prussian blue in addition to the property of facilitating ignition, like the soluble blue, in contents above 3-4%.

Ammonia Prussian blue is obtained by causing gaseous ammonia to react on insoluble Prussian blue. The rate of reaction between these 2 substances increases only up to 60°C. The evolved ammonia Prussian blue has a strong ammonia smell after cooling; however, this smell can be removed by heating for several hours at 70°C. The activity of odorless ammonia Prussian blues is no different than that of those with the odor.

By treating various insoluble Prussian blues, having different activities and obtained in different ways, with ammonia, ammonia blues with identical properties result.

Other ferro-cyanides used are nickel and copper ferro-cyanides.



All the above ferro- and ferri-cyanic "catalyzers" are added in quantities of 0-15 parts by weight to 100 parts by weight of propellant, preferably 1-4 parts to 100 parts by weight of propellant. They are active via absorption, primarily due to their dark color, and also via chemiluminescence of the iron atoms, excited  $C_2$  particles or  $-CN$  radicals, etc. [1, 36, 39, 44, 49, 60, 61, 63, 64, 65, 67, 80, 81, 87].

#### Nitrocompound

The organic "catalyzers" used are salts of picric and styphnic acids (2,4,6-trinitroresorcinol). They exert their action via exothermic decomposition or via chemiluminescence of the metals entering into the composition of the compounds. The picrates are: potassium (K), calcium (Ca), lithium (Li), chromium (Cr), ammonium ( $NH_4^+$ ), sodium (Na), copper (Cu), zinc (Zn), cadmium (Cd), nickel (Ni), aluminum (Al), iron (Fe), strontium (Sr), cesium (Cs), beryllium (Be), urea, n-heptylamine salts; tetraethylamine and N-methylpyridine picrates. The styphnates include: the salts of sodium (Na), lead (Pb), ammonium ( $NH_4^+$ ), silver (Ag), potassium (K), calcium (Ca), barium (Ba), rubidium (Rb), magnesium (Mg), pyridine, guanidine, guanyl urea and isopropyl amine.

Picrates and styphnates are added in amounts of 2-20% and their particle size is of the order of about 0.04-2 mm [36].

The influence of some of the above described catalyzers is given in Table 7.7 for a propellant based on a composition of 16.5% combustible component and 83.5% ammonium nitrate ( $NH_4NO_3$ ).

The combustible component composition is as follows:

	parts by weight
the copolymer, Bd/MVP 90:10	100
carbon black	22
stabilizer	3
di(butoxy-ethoxy)formal	20
MgO	5

TABLE 7.7. THE EFFECT OF SOME COMBUSTION "CATALYZERS" ON THE BURNING RATE OF A PROPELLANT WITH BINDER CONTAINING THE COPOLYMER, Bd/MVP 90:10

Propellant no.	Parts by weight of "catalyzer" to 100 parts by weight of "basic propellant"							Burning rate $\bar{r}$		
	Milori blue	$(\text{NH}_4)_2\text{Cr}_2\text{O}_7$	$\text{CuO} \cdot \text{Cr}_2\text{O}_3$	Disodium styphnate	CuO	Cu	Urea picrate	Dipotassium styphnate	at 42.4 $\frac{\text{kg}}{\text{cm}^2}$ [cm/sec]	at 70.3 $\frac{\text{kg}}{\text{cm}^2}$ [cm/sec]
1	2								0.366	0.533
2	2	4							0.565	0.711
3	2			4					0.438	0.561
4			4						0.315	0.463
5		4	4						0.472	0.628
6		4	4	4					0.739	0.942
7		6	4	4					0.704	0.819
8		2	4	4					0.518	0.711
9		4	2	4					0.653	0.858
10		4	8	4					0.678	0.897
11		4	4	2					0.571	0.749
12		4		4	4				0.599	0.770
13		4		4		4			0.610	0.749
14		4	4				6		0.721	0.895
15		4	4					4	0.714	0.895



This propellant was formed in a rod with a diameter of 0.475 cm and hardened at 82.2°C for 24 hours. These rods were cut into lengths, 17.78 cm long, entirely covered, except for the end, with a noninflammable substance, and placed in a pressure bomb under the desired pressure in a nitrogen atmosphere. The bomb was placed in a bath at a temperature of 21.1°C and the burning time of a 12.7 cm long rod was measured.

Table 7.8 presents some data, which also takes other picric or styphnic salts into account.

TABLE 7.8. THE EFFECT OF SOME PICRATES AND STYPHNATES ON THE BURNING RATE OF A PROPELLANT WITH BINDER CONTAINING THE COPOLYMER, Bd/MVP 90:10

Propellant number	$(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ , parts by wt. to 100 parts by wt. of "basic propellant"	$\text{CuO} \cdot \text{Cr}_2\text{O}_3$ , parts by wt. to 100 parts by wt. of "basic propellant"	Trinitrophenol salts	Parts by wt. to 100 parts by wt. of "basic propellant"	Burning rate $\bar{r}$	
					at 42.2 kg/cm <sup>2</sup> [cm/sec]	at 70.3 kg/cm <sup>2</sup> [cm/sec]
1	4	4	Urea styphnate	4.0	0.516	0.688
2	4	4	Urea picrate	6.0	0.571	0.777
			Potassium styphnate	4.0		
3	4	4	Dipicrylamine	6.0	0.571	0.749
4	4	4	Sodium picrate	10.0	0.920	1.168

The influence of some "catalyzers" according to data for propellants with the composition given in Table 7.9 can best be compared on the basis of Table 7.10, wherein it is evident that ammonium dichromate induces the greatest increase, while cupric chromite increases the burning rate by less than half. Sodium picrate equals the effect of cupric chromite only with additive quantities 2.5 times greater. On the other hand, all the "catalyzers" exhibit a greater increase in the burning rate when mixed together than would result from the sum of the increases for the individual constituents. Thus, a "catalyzer" mixture furnishes a synergic action [36].

Other organic compounds used as combustion "catalyzers" are: monosodium

TABLE 7.9. THE COMPOSITION OF SOME PROPELLANTS  
WITH BINDER CONTAINING THE COPOLYMER, Bd/MVP 90:10

Constituents	Composition (parts by weight)				
	1	2	3	4	5
Combustible component	16.5	16.5	16.5	16.5	16.5
$\text{NH}_4\text{NO}_3$ $\phi$ 40 $\mu$	83.5	83.5	83.5	83.5	83.5
$(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ $\phi$ 15 $\mu$	0	4.0	0	0	4.0
$\text{CuO} \cdot \text{Cr}_2\text{O}_3$ $\phi$ 3-4 $\mu$	0	0	4.0	0	4.0
Sodium picrate (0.23-0.15 mm, 65-100 American sieve)	0	0	0	10.0	10.0

TABLE 7.10 THE EFFECT OF SOME COMBUSTION "CATALYZERS" ON  
THE BURNING RATE OF THE PROPELLANTS GIVEN IN TABLE 7.9

Propellant no.	Burning rate $r$			
	at 42.2 kg/cm <sup>2</sup> [cm/sec]	increase in burning rate $\Delta r$ [cm/sec]	at 70.3 kg/cm <sup>2</sup> [cm/sec]	increase in burning rate $\Delta r$ [cm/sec]
1 (standard)	0.175	-	0.272	-
2	0.488	0.313	0.641	0.369
3	0.315	0.140	0.463	0.191
4	0.317	0.142	0.429	0.157
5	0.889	0.714	1.123	0.851

barbiturate (1-10%), pyridine N-oxide 1-5% (exothermic decomposition) and organic dyes [65, 67, 81].

#### Organic dyes

The organic dyes merit a broader discussion because they can successfully replace the inorganic "catalyzers".

These dyes are: aniline black, the indophenols and a different type of blue.

They all act by absorbing radiation because they all have deep colors, ranging to black. When added in amounts of approximately 2.5%, these dyes can increase the burning rate by 30-40%. In mixtures with inorganic "catalyzers", they exhibit a synergic action.

One of these indophenol dyes can be obtained by heating 10 parts by weight of 2,4-dinitro-4'-hydroxydiphenyl amine with 18 parts by weight of dry sodium tetrasulfide in 50-60 parts by weight of alcohol at a temperature of 135-145°C for 3-4 hours in an autoclave under a pressure of 8-10 atm. The alcohol is distilled off and the dye crystallizes from the mother solution.

However, commercial dyes such as: direct blues -- Pyrogene Direct Blue RL-CL and Pyrogene Direct Blue GLR-CL, Sulfogene Direct Blue BN, Sulfogene Brilliant Blue BGL and Sulfogene Navy Blue 4RCF Supra, are most frequently used.

TABLE 7.11. THE EFFECT OF ORGANIC DYES ON THE BURNING RATE OF PROPELLANTS WITH BINDERS CONTAINING CELLULOSE ACETATE

Dye (color index in parentheses)	Burning rate $\frac{r}{\text{cm}^2}$ at 70.3 kg/cm <sup>2</sup>		Burning rate increase [%]	n
	standard [cm/sec]	propellant studied [cm/sec]		
Sulfogene Direct Blue BN (956)	0.203	0.279	38	0.83
Sulfogene Brilliant Blue BGL (961)	0.203	0.279	38	0.78
Sulfogene Navy Blue 4RCF Supra (959)	0.203	0.254	25	0.76
Pyrogene Direct Blue RL-CL (956)	0.254	0.356	40	0.70
Pyrogene Direct Blue GLR-CL (959)	0.254	0.330	30	0.73

Table 7.11 gives their effect on the burning rate for a propellant of composition:

	%
cellulose acetate	5.8
ethylene glycol diglycolate	9.6
2,4-dinitro-diphenyl ether	9.6



Prussian blue

2.0

$\text{NH}_4\text{NO}_3$

73.0

in which 10% of the binder (which constitutes 2.5% of the propellant) is replaced by the dye [49].

#### Salts of aromatic amino-carboxylic acids

It was learned that during propellant combustion the inorganic "catalyzers" produce high-melting heavy metal oxides ( $\text{Cr}_2\text{O}_3$ ,  $\text{CuO}$ ,  $\text{Fe}_2\text{O}_3$ , etc.) which have a substantial corrosive effect on the nozzle (through friction caused by the expulsion of solid particles). On the other hand, potassium-group oxides have a lower melting and boiling or sublimation point, and they pass into the gaseous phase at the temperature of combustion. When a uniform (mass) discharge is necessary, the nozzle must not change its diameter nor undergo corrosion (for example, in gas generators). In that case potassium-group salts and amino-carboxylic acids are used as combustion "catalyzers"; these are, e.g., salts of o-aminobenzoic and anthranilic acids. The amount of these salts added is dependent on the binder, oxidizer and the desired burning rate; for ammonium nitrate and cellulose esters with a self-oxidizing plasticizer, it is 1-6% [113].

#### 7.2.2. Moderators

Very often it becomes necessary to decrease the burning rate in the case of a number of propellants, particularly those with perchlorate oxidizers. This is accomplished by adding a moderator. However, in most cases the substances that are moderators for rapidly burning propellants containing perchlorates are, at the same time, combustion "catalyzers" for propellants containing nitrates ( $\text{NH}_4\text{NO}_3$ , in particular). Accordingly, the term "moderator" should be taken to mean a substance which decreases the burning rate of propellants containing perchlorates. The application of moderators to propellants containing nitrates would be completely useless, because these propellants have such a low burning rate that most frequently it is

necessary to add combustion "catalyzers" in order to support combustion.

It is possible to distinguish 3 groups of moderators: salts of inorganic acids and hydroxylamines or semicarbazide, heteromolybdates and aliphatic diamine dinitrates.

Hydroxylamine or semicarbazide can serve as the moderator. However, their salts have proved to be better; in particular, these are:

$\text{NH}_2\text{OH} \cdot \text{HClO}_4$  - perchlorate

$\text{H}_2\text{N}-\text{CO}-\text{NHNH}_2 \cdot \text{HClO}_4$

$\text{NH}_2\text{OH} \cdot \text{HCl}$  - hydrochloride

$\text{H}_2\text{N}-\text{CO}-\text{NHNH}_2 \cdot \text{HCl}$

$2\text{NH}_2\text{OH} \cdot \text{H}_2\text{SO}_4$  - sulfate

$2\text{H}_2\text{N}-\text{CO}-\text{NHNH}_2 \cdot \text{H}_2\text{SO}_4$

$\text{NH}_2\text{OH} \cdot \text{H}_2\text{SO}_4$  - acid sulfate

$\text{NH}_2\text{OH} \cdot \text{HNO}_3$  - nitrate

$\text{H}_2\text{N}-\text{CO}-\text{NHNH}_2 \cdot \text{HNO}_3$

$3\text{NH}_2\text{OH} \cdot \text{H}_3\text{BO}_3$  - borate

$3\text{NH}_2\text{OH} \cdot \text{H}_3\text{PO}_4$  - phosphate

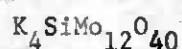
$2\text{NH}_2\text{OH} \cdot \text{H}_2\text{SiF}_6$  - fluorosilicate

These salts are added in amounts of 0.1-20 parts by weight to 100 parts by weight of propellant, preferably 0.5-10 parts by weight. As in the case of combustion "catalyzers", the moderators are ground together with the oxidizer.

Table 7.12 shows the action of hydroxylamine and semicarbazide hydrochlorides in a propellant having a composition: 15% copolymer 90/10 Bd/MVP and 85%  $\text{NH}_4\text{ClO}_4$  [114].

Phospho- and silico-molybdate compounds with the general formula  $\text{X}_n \text{Z}_a \text{Mo}_b \text{O}_c$ , where  $\text{X} = \text{NH}_4, \text{Na}, \text{K}, \text{Li}, \text{Rb}, \text{Cs}$ ;  $n$  = the valence of the  $\text{Z}_a \text{Mo}_b \text{O}_c$  anion, which may be 2-8;  $\text{Z} = \text{P}, \text{Si}$ ;  $a = 1.2$ ;  $b = 6-18$ ;  $c = 24-62$ , are good moderators.

In particular, these compounds are<sup>1</sup>:



- tetrapotassium-silico-12-molybdate

<sup>1</sup>See page 284



TABLE 7.12. THE EFFECT OF HYDROXYLAMINE AND SEMICARBAZIDE HYDROCHLORIDES ON THE BURNING RATE OF A PROPELLANT WITH BINDER CONTAINING THE COPOLYMER, Bd/MVF 90:10

Propellant no.	Moderator	Parts by wt. to 100 parts by wt. of propellant	Burning rate $r$		Moderation	
			at 21 kg/cm <sup>2</sup> [cm/sec]	at 70.3 kg/cm <sup>2</sup> [cm/aec]	at 21 kg/cm <sup>2</sup> [%]	at 70.3 kg/cm <sup>2</sup> [%]
1		-	2.286	3.505	-	-
2	HCl·H <sub>2</sub> NOH	2	1.245	1.854	46	47
3		-	1.651	-	-	-
4	HCl·H <sub>2</sub> N-CO-NHNH <sub>2</sub>	5	1.143	-	31	-

In propellants 1 and 2, the NH<sub>4</sub>ClO<sub>4</sub> is present with 2 particle sizes: 74 μ and 18 μ, 70 and 30%, respectively.

In propellants 3 and 4, particle sizes 200 μ and 40 μ, 70 and 30%, respectively.

(NH <sub>4</sub> ) <sub>4</sub> SiMo <sub>12</sub> O <sub>40</sub>	- tetraammonium-silico-12-molybdate
Na <sub>4</sub> SiMo <sub>12</sub> O <sub>40</sub>	- tetrasodium "
Rb <sub>4</sub> SiMo <sub>12</sub> O <sub>40</sub>	- tetrarubidium "
Cs <sub>4</sub> SiMo <sub>12</sub> O <sub>40</sub>	- tetracesium "
Li <sub>4</sub> SiMo <sub>12</sub> O <sub>40</sub>	- tetralithium "
Na <sub>3</sub> P <sub>3</sub> Mo <sub>12</sub> O <sub>40</sub>	- trisodium phospho-12-molybdate
K <sub>3</sub> P <sub>3</sub> Mo <sub>12</sub> O <sub>40</sub>	- tripotassium "
(NH <sub>4</sub> ) <sub>3</sub> P <sub>3</sub> Mo <sub>12</sub> O <sub>40</sub>	- triammonium "
(NH <sub>4</sub> ) <sub>5</sub> P <sub>5</sub> Mo <sub>9</sub> O <sub>32</sub>	- pentaammonium phospho-9-molybdate
Cs <sub>6</sub> SiMo <sub>9</sub> O <sub>32</sub>	- hexacesium silico-9-molybdate
(NH <sub>4</sub> ) <sub>7</sub> P <sub>7</sub> Mo <sub>6</sub> O <sub>24</sub>	- heptaammonium phospho-6-molybdate
K <sub>7</sub> P <sub>7</sub> Mo <sub>11</sub> O <sub>39</sub>	- heptapotassium phospho-11-molybdate
Na <sub>8</sub> SiMo <sub>12</sub> O <sub>42</sub>	- octasodium silico-12-molybdate

$(\text{NH}_4)_2\text{P}_2\text{Mo}_{12}\text{O}_{42}$  - diammonium 2-phospho-12-molybdate

$(\text{NH}_4)_6\text{P}_2\text{Mo}_{18}\text{O}_{62}$  - hexaammonium 2-phospho-18-molybdate

$\text{Na}_6\text{P}_2\text{Mo}_{18}\text{O}_{62}$  - hexasodium " "

Heteromolybdates are added in amounts of 0.1-15, preferably 0.2-5 parts by weight to 100 parts by weight of propellant. The effect of 2 heteromolybdates on a propellant with the composition: 15% copolymer 90/10 Bd/MVP and 85%  $\text{NH}_4\text{ClO}_4$  is given in Table 7.13.

TABLE 7.13. THE EFFECT OF HETEROMOLYBDATES ON THE BURNING RATE OF A PROPELLANT WITH BINDER CONTAINING THE COPOLYMER, Bd/MVP 90:10

No.	Moderator parts by weight to 100 parts by weight of pro- pellant	Burning rate $\bar{r}$			Moderation (%)		
		at 21.1 kg/cm <sup>2</sup> [cm/sec]	at 42.2 kg/cm <sup>2</sup> [cm/sec]	at 70.3 kg/cm <sup>2</sup> [cm/sec]	at 21.1 kg/cm <sup>2</sup>	at 42.2 kg/cm <sup>2</sup>	at 70.3 kg/cm <sup>2</sup>
1	- 0	1.753	2.769	3.581	0	0	0
2	$\text{Na}_4\text{SiMo}_{12}\text{O}_{40}$ 2	1.118	1.549	1.987	36	44	45
3	$\text{Na}_3\text{PMo}_{12}\text{O}_{40}$ 2	1.676	2.476	3.277	4	11	9

Diamine dinitrates with the general formula



where: R - an alkylene or alkenylene with 2-14 carbon atoms, R' - an alkyl with 1-4 carbon atoms, are effective moderators for propellants containing perchlorates.

The total number of carbon atoms in the molecule should not exceed 18. The nitrates of these amines are effective in small amounts (0.1-20 parts by weight to 100 parts by weight of propellant), are stable and do not yield harmful residues after burning.

In particular, they are the dinitrates of the following amines:

N,N,N',N'	- tetramethyl-2,3-diamine butane
N,N,N',N'	- tetramethyl-3,4-diamine hexane
N,N,N',N'	- tetramethyl-1,2-diamine ethane
N,N,N',N'	- tetramethyl-1,3-diamine propane
N,N,N',N'	- tetramethyl-1,8-diamine octane
N,N,N',N'	- tetramethyl-1,14-diamine tetradecane
N,N,N',N'	- tetramethyl-1,3-diamine dodecene-1
N,N,N',N'	- tetramethyl-1,6-diamine hexane
N,N,N',N'	- tetramethyl-1,3-diamine-2,2-dimethyl propane
N,N,N',N'	- tetramethyl-1,3-diamine-2-ethyl propane
N,N,N',N'	- tetramethyl-2,4-diamine octane
N,N,N',N'	- tetramethyl-1,3-diamine butane
N,N,N',N'	- tetramethyl-1,4-diamine butane
N,N,N',N'	- tetramethyl-2,5-diamine hexane
N,N,N',N'	- tetramethyl-1,4-diamine butene-2
N,N,N',N'	- tetramethyl-1,5-diamine tetradecane
N,N,N',N'	- tetramethyl-1,5-diamine-2,4-dimethyl pentane
N,N,N',N'	- tetramethyl-1,8-diamine-3,6-dipropyl octane
N,N,N',N'	- tetraethyl-1,3-diamine butane
N,N,N',N'	- tetraethyl-1,3-diamine decene-2
N,N,N',N'	- tetraethyl-1,2-diamine ethylene
N,N,N',N'	- tetra-n-propyl-1,3-diamine butane
N,N,N',N'	- tetra-i-propyl-1,4-diamine butane
N,N	- dimethyl-N',N'-diethyl-1,3-diamine butane
N,N	- dimethyl-N',N'-diethyl-1,10-diamine-2,8-dimethyl decane

Table 7.14 shows the effect of one dinitrate of these amines on a propellant of composition: 15% copolymer 90/10 Bd/MVP and 85%  $\text{NH}_4\text{ClO}_4$  (116).



TABLE 7.14. THE EFFECT OF N,N,N',N'-TETRAMETHYL-1,3-DIAMINO BUTANE NITRATE ON THE BURNING RATE OF A PROPELLANT WITH BINDER CONTAINING THE COPOLYMER, Bd/MVP 90:10

Propellant	N,N,N',N'-tetramethyl-1,3-diaminobutane (parts by weight to 100 parts by weight of propellant)	Burning rate $\bar{r}$			Moderation (%)		Size reduction $\text{NH}_4\text{ClO}_4$
		at 21.1 $\text{kg/cm}^2$ [cm/sec]	at 42.2 $\text{kg/cm}^2$ [cm/sec]	at 70.3 $\text{kg/cm}^2$ [cm/sec]	at 21.1 $\text{kg/cm}^2$	at 70.3 $\text{kg/cm}^2$	
1	-	1.600	-	2.781	-	-	70% 74 $\mu$
2	2	1.245	-	1.869	22	33	30% 15 $\mu$
3	-	1.524		2.743	-	-	70% 210 $\mu$
4	1	1.295	1.702	2.034	15	26	30% 40 $\mu$
5	5	1.219	1.524	1.829	20	33	

### 7.2.3. Burning rate modifiers

Depending on their amounts or methods of application, some substances may have a number of effects at the same time: they influence the burning rate; improve other properties of the propellant such as the mechanical strength, or increase the chemical energy reserves, etc. These substances may either increase or decrease the burning rate; and sometimes, depending on the other constituents, the same substance can cause either an increase or a decrease. This type of additive, used to vary the burning rate, is called "burning rate modifiers". There are frequently inaccuracies in the literature: in particular, the term "modifier" is used to mean "modifier of the exponent  $n$ ". One must distinguish between these 2 concepts because the first refers to variation of the burning rate at constant pressure while the second refers to variations in relation to the burning rate under different pressures of a propellant without a modifier.

Burning rate modifiers include different types and grades of carbon black; graphite; silicon dioxide; some powdered metals such as boron, magnesium, aluminum; and mixtures of these. Of course, the carbon blacks should be included among the

combustion "catalyzers"; nevertheless, it is customary to call them modifiers. This terminology can be supported by the fact that they are universally used, not as "catalyzers" but as fillers, to improve the mechanical properties of the propellant rather than to increase the burning rate. The latter also occurs, but it is only an auxiliary or secondary effect. Frequently, however, carbon blacks are added for the sole purpose of increasing the burning rate.

The mechanism of the action of carbon black has not been studied -- certainly there must be an absorption of the radiation. Moreover, the effectiveness of carbon black is a function of the degree of surface development. Thus, for example, activated charcoal from animal remains has proved to be the best -- undoubtedly because it has the most highly developed surface. We should mention other types of carbon black and carbon, such as channel (gas) black, furnace black, lampblack, petroleum coke and graphite.

Gas black results from the incomplete combustion of natural gas, furnace black from the partial combustion of gaseous hydrocarbons in a closed furnace, thermal furnace black from the decomposition of such hydrocarbons as acetylene in a superheated furnace; and lampblack is formed by burning liquid fuels such as petroleum, tars or the residues remaining after the distillation of petroleum. These carbon blacks contain a very small amount of ash (less than 0.5% and usually less than 0.15%). In addition, they are in the form of very small particles, 50-5000 Å, and contain certain amounts of adsorbed oxygen and hydrogen.

Petroleum coke should have less than 1% ash, it should be activated, and it must be reduced in size to a particle size of about 0.044 mm. Graphite is also subjected to grinding; it should contain no more than 5% ash.

Carbon blacks, graphite or petroleum coke are added to propellants in amounts of 1-10%; preferably, however, 2-6%. It should pass through at least a No. 20 Standard American Sieve (mesh: 0.84 mm), better through a No. 200 (mesh: 0.074 mm), and most preferably through a No. 325 (mesh: 0.044 mm).

Table 7.15 [1] illustrates the effect of the various carbon types on the



burning rate of a propellant of composition.

	%
cellulose acetate	4.75
2,4-dinitro-diphenyl ether	8.00
ethylene glycol diglycolate	8.00
insoluble Prussian blue	3.00
acetonyl acetone dioxime	2.30
carbon black	1-5
$\text{NH}_4\text{NO}_3$	69-73

It is evident from the table that the most effective carbons are those with well developed surfaces. A further increase in the amount of carbon produces no great changes in the burning rate. For example, a 400% increase in the amount of activated charcoal resulted in only an increase of approximately 50% in the burning rate in propellant Nos. 2 and 3 [1, 3, 43, 49, 61, 64, 65, 68, 77, 78, 81, 93].

TABLE 7.15. THE EFFECT OF VARIOUS CARBON TYPES ON THE BURNING RATE OF A PROPELLANT WITH BINDER CONTAINING CELLULOSE ACETATE

Propellant no.	Type of carbon	Carbon content [%]	Burning rate $r$ at 70.3 kg/cm <sup>2</sup> [cm/sec]	Increase in the burning rate [%]
1	Standard (without carbon)	-	0.356	-
2	Norit A (activated carbon), sieve 325 (mesh, 0.044 mm)	1	0.483	35
3	Norit A	5	0.559	57
4	Carbon black, sieve 325 (mesh, 0.044 mm)	1	0.483	35
5	Petroleum coke	0.8	0.432	21
	Carbon black	0.2	0.432	21
6	Graphite	1	0.406	14

It has been shown that silica in the form of a finely ground gel (10-20  $\mu$ ), added to increase the modulus of elasticity in the amount of 1-20 parts by weight to 100 parts by weight of binder, also induces a lowering of the burning rate (Table

TABLE 7.16. THE EFFECT OF  $\text{SiO}_2$  ON THE BURNING RATE

Propellant no.	Parts by weight to 100 parts by weight of copolymer		
	1	2	3
Copolymer Bd/MVP 90:10	100	100	100
Carbon black	20	20	20
$\text{SiO}_2$	0	1	3
$\text{NH}_4\text{NO}_3$	753	758	768
Di(butoxy-ethoxy-ethoxy)formal	20	20	20
Milor blue	18	18	18
AnO	3	3	3
Flexamine (stabilizer)	3	3	3
Aerosol OT (surface-active agent)	1	1	1
Sulfur	0.75	0.75	0.75
SA-113 (dithiocarbamate derivative)	1	1	1
Burning rate $\bar{r}$ [cm/sec]	0.419	0.409	0.268
Burning rate lowering [%]	-	2	12

7.16). It follows from the table that an addition of about 0.3%  $\text{SiO}_2$  lowers the burning rate by almost 12% [3].

It was also learned that some metallic elements, when added for the purpose of increasing the chemical energy reserves in the propellant, either increase or reduce the burning rate, depending on the amount of oxidizer. Thus, for example, boron decreases the burning rate when there is 82%  $\text{NH}_4\text{NO}_3$  in the propellant and increases it when there is a 92%  $\text{NH}_4\text{NO}_3$  content. This effect is exhibited not only by boron but also by magnesium (Mg), a mixture of boron with magnesium, mixtures of boron or boron with magnesium and with 50% of such elements as aluminum (Al), beryllium (Be) and lithium (Li). These substances are added to the propellant in amounts of 1-10%. The particle size should at least be below 50  $\mu$ ; it is better if it is below 20  $\mu$  and most preferable if it is below 10  $\mu$ . The effect of these metals on

TABLE 7.17. THE EFFECT OF HIGH-CALORIFIC METALS ON THE BURNING RATE OF SOME PROPELLANTS WITH BINDERS CONTAINING THE COPOLYMER, BUTADIENE-1,3

Components in parts by weight	Composition in parts by weight														
	Propellant no.	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Combustible component															
90/10 Bd-styrene	100														
carbon black	20	8													
Combustible component															
90/10 Bd/MVP	100														
carbon black	20														
stabilizer	3			6	6	6	4	6	6	6	6	6			
Combustible component															
90/10 Bd/MVP	100														
carbon black	20														
benzophenone	20														
SA-113 (accelerator)	1.0														
sulfur	0.75												17.5	17.5	
ZnO	3.00														
flexamine	3.00														
Combustible component															
90/10 Bd/MVP	100														
carbon black	22														
flexamine	3														
butarez-25*	48														
Chloro-fluoro polymer															
NH <sub>4</sub> NO <sub>3</sub> (stabilized with KNO <sub>3</sub> )		92	90	92	90	88	90	90	90	90	90	94	82.5	82.5	7
(NH <sub>4</sub> ) <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>		2	2	2	2	2	2	2	2	2	2	2	4	4	1
Boron (Ø 1 µ)		-	2	2	4	6	6	-	2	-	-	-	-	4	0.5
Magnesium (Ø 6-10 µ)				-	-	-	-	4	3	-	-	-	-	-	88
Magnesium-aluminum, 60:40 alloy				-	-	-	-	-	-	4	-	-	-	-	2
Aluminum				-	-	-	-	-	-	-	4	-	-	-	2
T o t a l		102	102	102	102	102	102	102	103	102	102	102	104	108	100

TABLE 7.17. (CONTINUED) DATA FOR A TEMPERATURE OF 23°C

Propellant no.	Burning rate $\bar{r}$				n	
	at 42.2 kg/cm <sup>2</sup> [cm/sec]	increase [%]	at 70.3 kg/cm <sup>2</sup> [cm/sec]	increase [%]	at 42.2 kg/cm	at 70.3 kg/cm
1 standard	0.302	-	0.401	-		
2	0.488	62	0.698	74		
3	0.498	34	0.737	43	0.70	0.76
4	0.610	64	0.884	71	0.65	0.71
5	0.688	85	0.971	83	0.65	0.67
6	0.742	100	1.054	104	0.70	0.69
7	0.549	48	0.762	48	0.60	0.71
8	0.666	80	0.991	92	0.71	0.78
9	0.447	20	0.640	22	0.61	0.73
10	0.350	-5	0.510	-1		
11 standard	0.371	-	0.516	-	0.61	
12 standard	0.372	-	0.510	-	0.71	
13	0.323	-13	0.467	-8	0.7	
14 standard	0.292	-	0.569	-	0.51	
15	0.569	94	0.871	53		

\*(See p. 266) This is a plasticizer -- liquid polybutadiene (polymerized with sodium in heptane) with a Saybolt viscosity of about 2500 seconds at 37.8°C.

the burning rate is given in Table 7.17.

Nonhardened propellants prepared in accordance with Table 7.17 were burned in a pressure bomb. The increase in the burning rate is almost directly proportional to the boron content, as is evident from the table. With each 2% boron addition, the burning rate increases by about 30% in the presence of about 90% oxidizer. Magnesium is less effective, and aluminum exhibits only a weak reduction in the burning rate; while a mixture of boron with magnesium is more effective than boron alone. In the presence of 82.5% oxidizer, boron reduces the burning rate [62].

#### 7.2.4. Other substances that affect the burning rate

This group includes those substances that do not have a direct effect on the burning rate, but act indirectly by improving the properties of other constituents. An improvement of this type is required primarily by propellants with the composition: ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) with various asphalts, tars or even pitches. In these propellants the oxidizer and the combustible component both have a low melting point and thus have a tendency to spread over the surface of the burning charge. This results in an insulation of the propellant from the flame, which more than once has caused the charge to stop burning or led to irregular combustion and low burning rate. In order to prevent this occurrence, thickeners are added to both the oxidizer and the combustible component. As a result, neither the oxidizer nor the combustible component has a tendency to spread after the melting point is reached, but rather maintain the consistency of paste. The burning becomes stable and the burning rate increases.

The thickening agents are generally inorganic colloidal substances such as carbon black, Prussian blue, jewelers' rouge, various types of natural earths (improved with -onium or hydrophobic compounds), and synthetic earths, e.g., zeolites (aluminum-sodium silicates with different  $\text{Na}_2\text{O}$  contents), oxides and hydroxides of silicon, aluminum, magnesium, vanadium, iron, alkaline-earth carbonates ( $\text{CaCO}_3$ ), etc.

Some of the best thickeners -- -onium earths -- are obtained by the reaction



of natural earths with quaternary ammonium salts in amounts of 25-100 milliequivalents to 1,000 g of earth. The following ammonium compounds are used: naphthylammonium chloride, di(cyclohexyl)-ammonium bromide, lauryl-dimethyl-ammonium chloride, tetraethane-ammonium bromide, octadecyl-ammonium iodide, lauryl-phosphonium bromide and dimethyl-dicetyl-ammonium bromide.

The natural earths are also improved by the adsorption of hydrophobic substances, such as primary, secondary and tertiary aliphatic amines with at least 10 carbon atoms in the chain (e.g., dodecylamine, hexadecylamine, octadecylamine and their mixtures), naphthylamine, pyridine, pyrimidine, tetrahydropyrimidine derivatives and polyamines and amide amines.

The various types of carbon black used here include furnace black with a surface area of  $3-100 \text{ m}^2$  per gram and with a particle size of  $0.4-0.5 \mu$ ; and gas black with a surface area of  $100-200 \text{ m}^2$  and with a particle size of  $0.2-0.4 \mu$ .

However, the best ones have proved to be colloids of the aerogel type. They have a surface area of the order of  $100 \text{ m}^2/\text{g}$  or more. They can be prepared by various methods, as, e.g., by burning  $\text{SiCl}_4$  to  $\text{SiO}_2$  or by solvent exchange. The latter method results in high porosity gels. The water in the inorganic hydrogel is replaced with alcohol and the resultant alcohol gel is heated in an autoclave above the critical temperature of alcohol. Then the finished aerogel is obtained after the pressure is lowered.

The method of adding the thickening agent to the ammonium nitrate is very important. For example, adding 5% jewelers' rouge or calcium silicate by mixing the dry substances has no effect on the viscosity of fused ammonium nitrate. On the other hand, when these same substances are added to a 50% aqueous solution of ammonium nitrate and the mixture obtained is then desiccated, the substance obtained is a paste above the melting point of the nitrate. Moreover, the mixture thus obtained does not readily separate from the asphalt at the melting point during the combustion process. In order to obtain very fine particles during the desiccation process, an immiscible liquid in the amount of 1-5% (in relation to the solid

fraction) is added to the solution in question along with an emulsifying agent. The resultant emulsion is desiccated and then the remaining liquid is driven off.

The addition of a thickener to one phase of the propellant is not sufficient. It is better if the oxidizer and the combustible component are both treated in the above manner.

If 15% asphalt is mixed with 85% ammonium nitrate, the flame is capable of being extinguished very readily. An addition of 1% of the reaction product of bentonite (a type of natural earth) with dimethyl-diethyl ammonium chloride, available under the trade name "Benton 34", to asphalt results in stable combustion with a rate of 0.152 cm/sec. Moreover, the addition of thickeners to ammonium nitrate increases the burning rate nearly 3 times [44].

### 7.3. Modifiers of the Coefficients $n$ , $\pi_p$ , and $u$

The literature contains comparatively little data on substances which affect the coefficients,  $n$ ,  $\pi_p$ , and  $u$ . Undoubtedly, this is the result of governmental or industrial secrecy due to the fact that these coefficients are decisive in the ballistic properties of propellants.

So far, 5 groups of compounds have been mentioned that affect the above coefficients. They are plumbous salts of the higher fatty acids; polychromates (already discussed in section 7.2.1) and chromites; calcium and barium phosphates; oximes and heteromolybdates.

Obviously most important are the substances which influence the coefficient  $n$  in the equation  $\underline{r} = \underline{a} p^n$ . The influence of the coefficients  $\pi_p$  and  $u$  depends on the temperature difference,  $\Delta t = (t_1 - t_0)$ , in which  $t_0$  is the standard temperature and  $t_1$ , the real temperature of the propellant. Because standard temperature is usually room temperature or relatively close to it,  $\Delta t$  will either be equal to zero or have a small value. In other words, the influence of the coefficient  $\pi_p$  on the pressure and that of the coefficient  $u$  on the burning rate are negligible at temperatures close to standard temperature; consequently, substances which act to change the

values of these coefficients induce no real changes in the burning rate or the pressure under these conditions. The problem assumes a greater importance only with higher  $\Delta t$  values.

On the other hand, changes in the coefficient  $n$  under the influence of various substances are essential and very important. After all, it is frequently desirable to lower the value of this coefficient. A decrease of this type induces a smaller variation in the burning rate as a function of the pressure and, consequently, the combustion becomes more stable. Obviously, it is most advantageous to achieve the so-called plateau effect, where the burning rate remains the same ( $n = 0$ ) for a definite pressure range. In that case, even rather significant random variations in the pressure (taking place within the given pressure range) do not cause a variation in the burning rate, which is undoubtedly quite advantageous.

Substances which radically reduce the coefficient  $n$  and frequently also result in the plateau effect are plumbous salts of organic acids such as the N,N-di(2-ethyl-hexyl)- $\beta$ -aminopropionate, 12-ketostearate, 9- or 10-acetamide stearate, cyclohexyloxyacetate, butoxy acetate, etc. The acids should have at least 6 carbon atoms in the chain.

In amounts of about 3% of the propellant, these salts induce a practically constant burning rate in the pressure range, 70.3-140.6 kg/cm<sup>2</sup> (Table 7.18) for a propellant of composition:

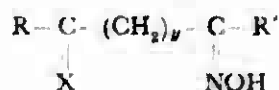
	%
nitroglycerin	24.7
nitrocellulose	57.8
triacetyne	9.2
dioctyl phthalate	3.3
2-nitro-diphenylamine	1.7
plumbous salt	3.3

To be sure, the example in Table 7.18 concerns colloidal propellants, but it is also possible to achieve the plateau effect in composite fuels, particularly those based on ammonium perchlorate [6, 67, 77].

TABLE 7.18. THE EFFECT OF LEAD SALT ON THE BURNING RATE OF A NITROCELLULOSE PROPELLANT

	Burning rate $\bar{r}$ at 70.3-140.6 kg/cm <sup>2</sup>	
	at 21.1°C [cm/sec]	at 60°C [cm/sec]
N,N-di-2-ethyl-hexyl- $\beta$ -amino propionate	0.838-0.99	0.838-0.991
12-ketostearate	0.660-0.838	0.813-0.940
Basic 12-ketostearate	0.711-0.889	0.813-0.940
9(10)-acetamide stearate	0.686-0.736	0.787-0.864
Cyclohexyloxy acetate	0.864-0.864	1.09 -1.07
Butoxy acetate	0.940-0.864	0.940-0.914
Tetraphenylide	0.737-0.991	0.889-1.19

Oximes, particularly those in which the oxime group or groups are bound with acyclic carbon atoms, are especially effective in lowering the  $\bar{n}$  value. Cyclic oximes, such as benzoic or salicylic aldehyde derivatives, have proved to be excellent. In this respect, the oximes that are generally better are those with the formula:



where: R and R' =  $-\text{CH}_3$ ,  $-\text{C}_2\text{H}_5$  or H;  $y = 0-2$ ;  $-\text{X} = -\text{O}$ ,  $-\text{NCH}$ . The representatives here are acetonylacetone dioxime or monoxime and succinic aldehyde dioxime.

Acetonylacetone monoxime and dioxime are formed by the reaction of acetonylacetone with a hydroxylammonium salt (sulfate) in stoichiometric quantities in the presence of a strong base in aqueous solution at a temperature of 65-70°C. After reacting, the mixture is cooled and stirred until room temperature is reached; then it is drained and, after washing with a small amount of water, is subjected to

drying.

Oximes are used in amounts of 1-4% of the propellant, and they not only reduce the exponent  $n$ , but also facilitate ignition of the propellant. Oximes are mixed with the binder before the oxidizer is added.

The effect exerted by oximes on the exponent  $n$  is shown by a propellant of composition:

	%
cellulose acetate	4.75
2,4-dinitro-diphenyl ether	8.00
ethylene glycol diglycolate	8.00
insoluble Prussian blue	3.00
acetylacetone dioxime	2.30
$\text{NH}_4\text{NO}_3$	73.95

in which  $n = 0.58$ , and without the dioxime,  $n = 0.8$  [1, 49].

Phosphates, pyrophosphates and metaphosphates of calcium and barium are very effective in lowering exponent  $n$  when added in amounts of 0.5-2%. The coefficients  $\pi_p$  and  $u$  are lowered at the same time by them. This action is given in Table 7.19 for a propellant of composition:

	A	B	C
	%	%	%
$\text{NH}_4\text{NO}_3$	75.00	72.79	76
$(\text{NH}_4)_2\text{Cr}_2\text{O}_7$		1.99	
$\text{CuO} \cdot \text{Cr}_2\text{O}_3$			0.15
polyester	12.35	9.79	14.11
diethylene glycol	47%		
adipic acid	49.45%		
maleic anhydride	3.55%		
styrene	12.35	2.44	8.59
cumene hydrogen peroxide	0.25		0.25
tertiary butyl catechol		0.25	0.40
methyl acrylate		12.22	
methyl-ethyl ketone peroxide		0.49	
sodium salt of dioctyl-sulfo-succinic acid (wetting agent)			0.50



lecithin

A  
0.05B  
0.03C  
%TABLE 7.19. THE EFFECT OF PHOSPHATES ON THE COEFFICIENTS  $u$ ,  $\pi_p$  AND  $n$  FOR PROPELLANTS WITH A POLYESTER-STYRENE BINDER

Propellant	Modifier	%	$u$ [Ar%/1°C]	$\pi_p$ [Δp%/1°C]	$n$	Pressure [kg/cm <sup>2</sup> ]
A	-	-	0.22	0.40	0.44	35.15
A	-	-	0.27	0.49	0.44	70.3
A	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	1	0.16	0.22	0.22	35.15
A	"	1	0.20	0.25	0.22	70.3
A	"	1	0.13	0.16	0.21	35.15
A	"	1	0.18	0.23	0.21	70.3
A	"	0.5	0.22	0.34	0.39	35.15
A	"	0.5	0.23	0.23	0.0	70.3
A	"	2	0.13	0.18	0.31	35.15
A	"	2	0.18	0.27	0.31	70.3
A	-	-	-	0.49	0.45	35.15
A	Ba <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	1	-	0.31	0.38	35.15
B	-	-	0.38	0.74	0.50	70.15
B	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	0.5	0.14	0.29	0.35	70.15
C	-	-	0.38	0.72	-	56.24
C	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	1	0.25	0.54	-	56.24
C	-	-	0.54	0.76	-	56.24
C	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	1	0.29	0.38	-	56.24
C	Ca <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	1	0.34	0.45	-	56.24

It is evident from this that calcium phosphate is the better one; in amounts of 1%, it lowers the coefficient  $u$  by about 30-60%, the coefficient  $\pi_p$  by about 40-60% and the exponent  $n$  by about 50% [94].

As already mentioned (section 7.2.1), when added in amounts of about 1% to propellants based on ammonium perchlorate and on polyester with styrene, the poly-

TABLE 7.20. THE EFFECT OF HETEROMOLYBDATE ON THE BURNING RATE AND COEFFICIENT FOR PROPELLANTS WITH BINDERS CONTAINING THE COPOLYMER, Bd/MVP 90:10

Propellant no.	Modifier parts by wt. to 100 parts by wt. of propellant	Burning rate $\bar{r}$ at 21°C		$\pi_p$ at 70.3 kg/cm <sup>2</sup>			Decrease in $\pi_p$ [%]		
		at 42.2 kg/cm <sup>2</sup> [cm/sec]	at 70.3 kg/cm <sup>2</sup> [cm/sec]	at -57 to 21°C [%/°C]	at 21 to 77°C [%/°C]	at -57 to 77°C [%/°C]	-57-21°C	21-77°C	-57-77°C
1	-	1.150	0.226	0.297	0.317	0.308	-	-	-
2	Na <sub>4</sub> SiMo <sub>12</sub> O <sub>40</sub>	0.262	0.328		0.252		-	20	-
3	"	0.274	0.371		0.227		-	28	-
4	"	0.292	0.371		0.144		-	55	-
5	Na <sub>6</sub> P <sub>2</sub> Mo <sub>18</sub> O <sub>62</sub>	0.236	0.311		0.198		-	37	-
6	"	0.236	0.317		0.216		-	32	-
7	"	0.224	0.282		0.234		-	26	-
8	"	0.287	0.363		0.198		-	37	-
9	V <sub>2</sub> O <sub>5</sub>	0.302	0.412	0.216	0.234	0.227	27	26	26
10	"	0.343	0.434	0.216	0.09	0.160	27	72	48
11	"	0.206	0.325	0.144	0.234	0.176	51	26	43
12	V <sub>2</sub> O <sub>5</sub>	0.236		0.00	0.162	0.077	100	49	75
	Na <sub>4</sub> SiMo <sub>12</sub> O <sub>40</sub>								
13	V <sub>2</sub> O <sub>5</sub>	0.260		0.144	0.09	0.117	51	72	62
	Na <sub>4</sub> SiMo <sub>12</sub> O <sub>40</sub>								
14	V <sub>2</sub> O <sub>5</sub>	0.371		0.162	0.126	0.144	54	60	54
	Na <sub>4</sub> SiMo <sub>12</sub> O <sub>40</sub>								

chromates lower the coefficient  $u$  by about 15-40%,  $\pi_p$  by about 30-40% and  $n$  by about 20%.

The best chromite is cupric chromite,  $\text{CuO} \cdot \text{Cr}_2\text{O}_3$ ; it lowers the exponent  $n$  by an average of about 20%, sometimes up to 50%. The other chromites are less effective.

The heteromolybdates mentioned in section 7.2.2 proved to be very effective modifiers of the coefficient  $\pi_p$ . At the same time, they are moderators for perchlorate propellants and "combustion catalyzers" for nitrate propellants.

Together with  $\text{V}_2\text{O}_5$ , the heteromolybdates exhibit a synergic action in lowering the coefficient  $\pi_p$ .  $\text{NiO}$ ,  $\text{CoO}$ ,  $\text{TiO}_2$ , etc. have the opposite effect in that they tend to increase the  $\pi_p$  value. The heteromolybdates are added in amounts of 0.1-6 parts by weight to 100 parts by weight of propellant. If a modifier composed of  $\text{V}_2\text{O}_5$  and heteromolybdate is used, their ratio is 0.5 to 4.0 respectively.

The reaction of 2 heteromolybdates on a propellant of composition: 16.5% copolymer 90/10 Bd/MVP and 83.5%  $\text{NH}_4\text{NO}_3$ , is given in Table 7.20, wherein it is evident that a greater addition of modifier does not always result in a greater lowering of coefficient  $\pi_p$  and that the best modifiers are mixtures of heteromolybdates with vanadium pentoxide [117].

#### 7.4. Substances that Facilitate Ignition

There are many propellants that present difficulties during ignition. Most frequently, these are propellants in which asphalt, pitch or other petroleum processing products enter into the composition. In that case, the addition of substances that facilitate ignition is imperative. These are highly polar compounds containing nitrogen as oxides of amines  $\text{R}_3\text{NO}$ , nitriles, imines  $\text{R}=\text{NR}'$ , oximes  $\text{RR}'=\text{NOH}$ , where  $\text{R}$  represents paraffin, olefin, aromatic and naphthenic radicals and  $\text{R}'=\text{H}$ , organic radicals. In addition to these, the compounds may contain  $-\text{NO}_2$ ,  $-\text{O}-\text{NO}_2$ ,  $-\text{O}-\text{NO}$ ,  $-\text{NO}$ ,  $-\text{Cl}$ ,  $-\text{Br}$ ,  $-\text{NH}_2$ ,  $-\text{O}$ ,  $-\text{OH}$ ,  $-\text{N}_2-$ ,  $-\text{NH}-\text{NH}_2$  groups, etc. The above substances can be added to asphalt in amounts of 1-10%.

Carbon black, which is particularly effective in the presence of asphalt, also

merits attention as a substance which facilitates ignition. It is added in amounts of 1-3% of the propellant [95].

### 7.5. Surface-active Compounds

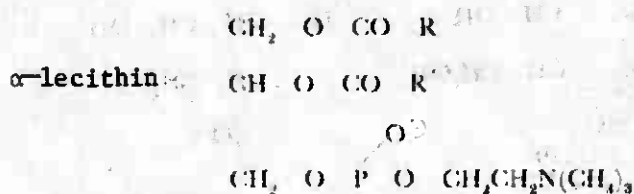
As already mentioned, surface-active agents permit an increase in the fluidity of the unhardened propellant and, as a result, make it possible to introduce new batches of oxidizer, usually about 30% more than when surface-active agents are not used. Moreover, they increase the stability of the dispersion and also stabilize the propellant. Because they act chiefly by increasing the coefficient of spreading, they are frequently called wetting agents. Quantitatively speaking, there are a great many surface-active agents; however, only a few of them are suitable for rocket propellants. The literature contains only scanty data on these specific substances, which is undoubtedly due to industrial secrecy.

Among the wetting agents used in rocket propellant production, there are 2 groups of surface-active agents: ionogenic and nonionic.

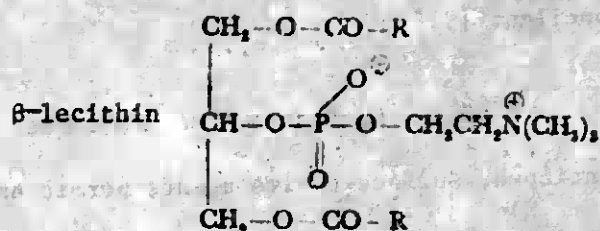
The ionogenic agents include such substances as: Aerosol OT, Duomeen C Diacetate, Onyxide and lecithin.

Aerosol OT is the sodium salt of the dioctyl ester of sulfo-succinic acid. Duomeen C Diacetate is the product of the reaction of acetic acid with the monosalt of trimethylene diamine and of acids with coconut oil. Onyxide is dimethyl-diethyl ammonium bromide.

Lecithins are ampholytic wetters because they contain both cations of quaternary nitrogen atoms and anions of oxygen atoms bound with phosphorus atoms



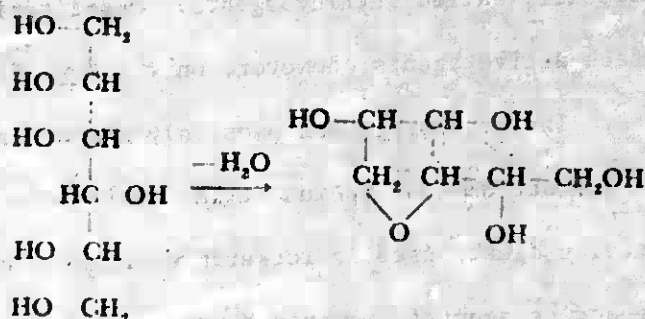




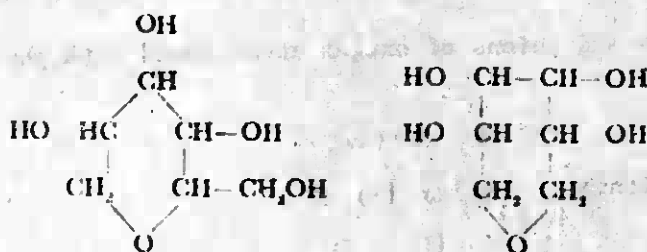
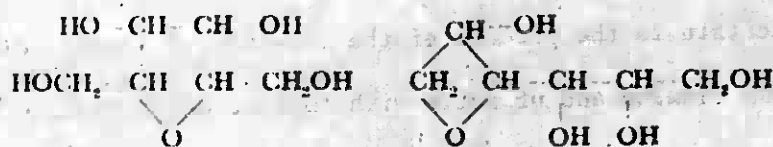
where R-COOH are the higher fatty acids [5, 49, 63, 64, 87, 88, 91, 92, 94].

The most important nonionic wetters include sorbitan and polyglycol derivatives.

Sorbitans are compounds which result from the dehydration of sorbite



The above compound is the principal dehydration product; other secondary products are formed, such as



The esters of sorbitans and oleic acid are particularly useful. It is better if only a portion of the -OH groups undergoes esterification, in particular, one or 2, no more than 3. The so-called Arlacel C has an average of 1.5 oleic acid mole-



cules to 1 sorbitan molecule. It is an oil at a temperature of 25°C, has a sp. gr. of 0.95-1.00 g/cm<sup>3</sup>, an ignition temperature of 232°C, a combustion temperature of 299°C and a viscosity of 900-1000 cp. Span 85, sorbitan trioleate, has a viscosity of 100-250 cp at 25°C, a sp. gr. of 0.92-0.98, an ignition temperature of 260°C and a combustion temperature of 299°C.

The above esters are obtained by heating oleic acid and sorbitans in the appropriate molar ratios in a carbon dioxide atmosphere at a temperature of 260°C [96]. The products obtained by the reaction of partial esters of sorbitans with ethylene oxide or with other alkylene oxides are also used.

The polyglycols are obtained by polymerization of alkylene oxides in the presence of small quantities of glycol. The copolymers of 2 alkylene oxides and polyglycol esters are particularly useful.

The so-called Pluronic L-62 has the following diagrammatic formula



It is obtained by polymerization of propylene oxide in the presence of sodium hydroxide (NaOH) until the molecular weight  $M = 1500-1800$  is reached and by a subsequent copolymerization with ethylene oxide and ethylene glycol until a value of  $M = 2000$  is reached. This is a liquid with a viscosity of 300-500 cp at 25°C.

Another wetting agent, Nonisol-250, is the monocaster of polyethylene glycol with a molecular weight of  $M \approx 1000$  and carbon atom numbers of 12-20 in the acids.

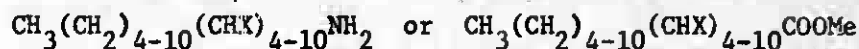
All the above surface-active agents are employed in very small amounts, usually 0.05-0.5%, sometimes up to 1%, most preferably 0.1-0.2% of the entire propellant [43, 65, 81].

## 7.6. Hydrophobic Substances

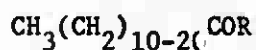
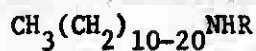
Most solid rocket propellants are based on ammonium nitrate or on ammonium perchlorate. Both of these oxidizers have a very annoying property: they are hygroscopic. In order to eliminate this disadvantage, it is imperative that the

oxidizer crystals be coated with hydrophobic substances, which protect against the absorption of moisture as well as against agglomeration.

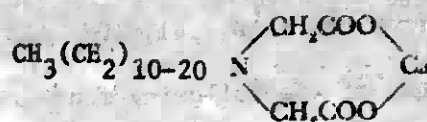
Vaseline or other mineral or natural fats have long been used for this purpose. However, an oxidizer prepared in this manner cannot bear the activity of temperatures which are of the order of several score degrees Celsius because the protective coating melts and runs off the crystals. In the new methods, substances composed of petroleum hydrocarbons or synthetic substances such as silicones, esters and chlorinated hydrocarbons with a flow temperature above 90°C and with a hardening temperature at about -20°C are used. In addition, these substances are thickened by the soaps (known for their hydrophobic properties) of such metals as calcium (Ca), barium (Ba), lead (Pb) or lithium (Li). A mixture thus formed is dissolved in benzine and the solvent is evaporated off after the addition of the oxidizer. For example, 10-30% barium soap is mixed with 70-90% of the above-mentioned mineral or synthetic substances. A 0.25-2% solution of this mixture in benzine with a bp of 80-110, 110-140 or 140-200°C is formed. After mixing with the oxidizer, the solvent is driven off at a temperature of 50°C and under a pressure of 10 mm Hg. The hydrophobic coating thus obtained is resistant within the temperature range, -65 to 250°C [97]. Other hydrophobic substances are products substituted with halogens



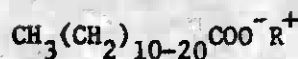
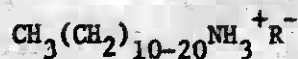
where X = the halogen and Me = the metallic cation  
or the condensation products



R = aromatic amine: benzoyl, naphthoyl, mono-, di and tri-nitrobenzoyl, nitronaphthoyl, phenyl, mono-, di- and tri-nitrophenyl, naphthyl, nitronaphthyl, pyridyl, phenoxyl, mono-, di- and tri-nitrophenoxyl, naphthoxyl, mono- and tri-nitronaphthoxyl. They can also be compounds of the type



or organic salts of bases and acids with long-chain fatty acids or amines



where:  $\text{R}^-$  = anions: benzoic, trinitrobenzoic, phenolic, picric, acetate, nitrate, chloride and complex anions of nitrotrimethyl methane with boric acid and tetramethyl methane with boric acid.

$\text{R}^+$  = aliphatic or aromatic ammonium, pyridine, etc. cations.

Primary, secondary and tertiary aliphatic amines with more than 10 carbon atoms in the chain are also suitable as hydrophobic substances, for example: dodecylamine, hexadecylamine, octadecylamine and aromatic amines and derivatives of heterocyclic compounds such as the derivatives of pyridine, pyrimidine, tetrahydropyrimidine, etc. [44, 97, 98].

#### 7.7. Substances that Facilitate Extrusion of the Grain

Composite propellants frequently have a high oxidizer content, ranging to 86-94%. Moreover, these propellants also contain other solid substances (metallic elements and others), which often lower the combustible component content down to 3.5%. It becomes evident that the extrusion of such mixtures is either impossible or fraught with formidable difficulties. Various types of waxes, mineral oils, etc. have long been employed to facilitate extrusion. However, highly chlorinated and fluorinated liquid polymers have proved to be the most effective. An addition of only 0.1-2.0% of them frequently results in a several hundred percent improvement in extrusion.

The halogen polymers used here should contain 2-4 carbon atoms in the monomer molecule and not more than 1 hydrogen atom to 1 carbon atom. These polymers are

generally obtained by the polymerization of monomers at an elevated temperature in the presence of organic peroxides [100, 101, 102, 110].

Polymers and copolymers of the following monomers are especially suitable:

perfluoromonochloro ethylene	perfluoromonochloro butene
perfluoro butadiene	perfluoro cyclobutene
perfluoro ethylene	perfluoro butene
perfluoro chloroprene	difluoro-dichloro ethylene (different isomers)
1,1-difluoro-2,3,3-trichloro propene-1	<u>sym</u> -difluoro ethylene
1,1-dichloro-2,3,3-trifluoro propene-1	<u>asym</u> -difluoro ethylene
1,1-difluoro-2-chloro ethylene	<u>asym</u> -dichloro ethylene
1-chloro-1,2-difluoro ethylene	1,1-difluoro-2-chloro propene-1
1,1-difluoro-3,4,4-trichloro butene-1	

copolymers 80:20 or 90:10 of perfluoromonochloro ethylene with asym-difluoro ethylene

75:25 of perfluoro ethylene with asym-dichloro ethylene

80:20 of perchloro ethylene with asym-difluoro ethylene

the prefix "per" signifies the substitution of all the hydrogen atoms by the given halogen atom.

The following propellants illustrate grain extrusion facilitation by the addition of halogen polymers:

Three propellants were prepared according to the following compositions:

	A	B	C
	%	%	%
copolymer 90/10 Bd/MVP	7	5	5
NH <sub>4</sub> NO <sub>3</sub> (stabilized with 10% KNO <sub>3</sub> )			
particle size, 60 μ	92	92	91
(NH <sub>4</sub> ) <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> , particle size, 18 μ	1	1	1
butarez-25 (plasticizer)	-	2	2

liquid halogen polymer<sup>2</sup>

A	B	C
%	%	%
-	-	1

In propellant B the liquid polybutadiene is mixed with the copolymer for 5-6 minutes and the oxidizer is slowly incorporated along with the catalyzer. In propellant C the halogen polymer is mixed with the oxidizer and the catalyzer and only then is incorporated into the binder with the plasticizer. The propellants obtained are extruded through an opening having a diameter of 1.27 cm and under a pressure of 675 kg/cm<sup>2</sup> and the rate of extrusion in cm/min is measured.

For propellant A this rate is insignificant, for propellant B it is 19 cm/min and for propellant C, 68.6 cm/min.

Table 7.21 presents the properties of the most frequently employed trifluoro-chloro ethylene polymers, bearing the trade names: Kel-F oil No. 1, No. 3 and No. 10 [62, 111].

TABLE 7.21. THE PHYSICAL PROPERTIES OF SOME TRIFLUORO ETHYLENE POLYMERS

	Kel-F oil no. 1	Kel-F oil no. 3	Kel-F oil no. 10
Mol. wt.	500	630	780
Color	colorless	colorless	colorless
Viscosity in centistokes at 38°C	3	25	220
at 99°C	1	3	10
Flow point, °C	< -57	-43	-1
Sp. gr. $d_4^{20}$	1.86	1.93	1.96

<sup>2</sup>See page 284



#### Footnotes

1. to p. 258. Detailed data on the structure, properties and preparation of these compounds is contained in the work by Killeffer and Linz: Molybdenum Compounds. Interscience Publishers, New York (1952).
2. to p. 283. Poly-trifluorochloro ethylene, bp  $110^{\circ}\text{C}$  at 1 mm Hg and flow point below  $-57^{\circ}\text{C}$  (trade name: Kel-F oil No. 1).

### III. EXAMPLES OF SOLID ROCKET PROPELLANTS

As already stated, the available publications provide limited data on the production or composition of solid rocket propellants. Due to the complex technological processes involved, the fact that the precise composition of a propellant has been furnished does not in the least mean that it is possible to prepare it. This problem is unusually difficult, and it is well known that even with an established composition and technological process, it is not always possible to obtain charges with identical ballistic properties. Reference is made below to some solid propellants and general data is provided concerning their composition and the processes involved in preparing the constituents and the propellants themselves. Although the examples cited can play an important role in orienting the reader and indicating what possibilities may be eliminated in the designing of propellants, they cannot be treated as specific guidelines.

The classification of propellants into groups is carried out on the basis of the binding substances. Nevertheless, there are difficulties involved in the classification of some propellants because of the composite nature of the binding constituent. Classification on the basis of the oxidizer employed would not be advantageous because generally there are only 3: ammonium nitrate, ammonium perchlorate and potassium perchlorate; accordingly, a classification of this type would be too general.

## 8. PROPELLANTS WITH SYNTHETIC POLYMERS AND POLYCONDENSATES

### 8.1. Propellants with Epoxy-Polyamide Resins

#### Examples of solid rocket propellants<sup>1</sup>

##### Propellant 1

###### (a) Polyamide

19 parts of sym-dimethyl urea and 56 parts of linoleic acid dimer are placed in a vessel with heating and cooling, with a mixer, reflux condenser and distillation unit. It is heated at 149°C for 24 hours, thus distilling off the water. The viscosity of the condensate is 68,000 cp at 66°C.

###### (b) Epoxy resin

Triethylene glycol diglycidyl ether. It is obtained by the reaction of 1,2-epoxy-3-chloropropane with triethylene glycol in a molar ratio of 2:1 in the presence of NaOH.

74 parts of triethylene glycol diglycidyl ether are added to the polyamide at 60°C. The resin obtained is mixed with 222 parts of  $\text{NH}_4\text{ClO}_4$  containing 1%  $\text{Fe}_2\text{O}_3$ . The mixing is continued for about 15 minutes at 60°C and the unhardened propellant is cast into forms. The whole batch is subjected to the action of decreased pressure in order to rid the propellant of air inclusions. When the viscosity at 60°C reaches 80,000-200,000 cp, the temperature is raised to 70°C and the propellant hardens for 10 hours. The burning rate without  $\text{Fe}_2\text{O}_3$  is 0.726 cm/sec; with 1%  $\text{Fe}_2\text{O}_3$ , it is 1.298 cm/sec.

Equally good results are obtained with the polyamide having the amine:acid molar ratio of 3:1 (26 parts of sym-dimethyl urea instead of 19 parts).

##### Propellant 2

(c) Polyamide as in propellant 1.

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<sup>1</sup>See page 325



(b) Epoxy resin -- the product of the reaction of epichlorohydrin with glycerin in the molar ratio of 2:1.

One part of polyamide is mixed with 5 parts epoxy resin and with 14 parts of  $\text{NaClO}_4$  and the same procedure is followed as in propellant 1.

#### Propellant 3

##### (a) Polyamide

A mixture of 14 parts of sym-dimethyl urea with 10 parts of di(4-aminophenyl) methane is slowly added (for 15 hours) to 56 parts of the linoleic acid dimer  $\text{C}_{34}\text{H}_{62}(\text{COOH})_2$  at  $177^\circ\text{C}$ . This is heated until viscosities of 30,500 cp at  $18^\circ\text{C}$  and 4400 cp at  $66^\circ\text{C}$  are attained.

##### (b) Epoxy resin as in propellant 1.

One part of each of the 2 resins is mixed with 6 parts  $\text{NH}_4\text{ClO}_4$  (with 1%  $\text{Fe}_2\text{O}_3$ ) and the mixture is hardened as in propellant 1. A mixture of ammonium perchlorate having 2 comminutions (70% of 0.1-30  $\mu$  and 30% of 50-200  $\mu$ ) is used.

#### Propellant 4

##### (a) Polyamide

25 parts of N-hexyl-N'-octyl urea is condensed with 9 parts of oxalic acid.

##### (b) Epoxy resin

1,2-epoxy-3-bromohexane with ethylene glycol in a molar ratio of 2:1 is subjected to condensation.

The polyamide is mixed with 3 parts epoxy resin with 0.01 parts tricresyl phosphate and with 8 parts  $\text{Ca}(\text{ClO}_4)_2$  (containing 1%  $\text{MgO}$ ). This propellant contains amine and acid in a molar ratio of 1.5:1.

#### Propellant 5

##### (a) Polyamide as in propellant 3.

(b) Epoxy resin -- product of the reaction of 1,2-epoxychloropropane with glycerin.

5 parts of the polyamide, 1 part of glycerin diglycidyl ether and 1 part of castor oil (plasticizer) are mixed with 28 parts  $\text{KClO}_4$  (containing 5%  $\text{Fe}_2\text{O}_3$ ).

#### Propellant 6

##### (a) Polyester-polyamide resin

20 parts of sebacic acid are heated for 15 hours with 20 parts of polyethylene glycol (mol. wt.  $\sim 400$ ) in a vessel with a reflux condenser and in a nitrogen atmosphere in the presence of 0.5%  $\text{ZnCl}_2$ . Then, 19 parts of sym-dimethyl urea are added and it is heated for another 15 hours, after which the water is distilled off. The viscosity of the product obtained is 100,000 cp at  $18^\circ\text{C}$  and 43,000 cp at  $46^\circ\text{C}$ .

##### (b) Epoxy resin -- triethylene glycol diglycidyl ether.

One part of each of the 2 resins are mixed with 7.5 parts of  $\text{NH}_4\text{ClO}_4$  (containing 0.1%  $\text{Fe}_2\text{O}_3$ ).

#### Propellant 7

##### (a) Polyamide

Sym-didodecyl urea and cetylmalonic acid in a molar ratio of 1.5:1 are subjected to condensation.

(b) Epoxy resin -- the product of the reaction of 1,2-epoxy-3-bromododecane with 1,2-dihydroxy-eicosane in a molar ratio of 2:1.

40 parts of the polyamide, 7 parts of the epoxy resin and 1 part of triethyl acetyl citrate are mixed with 33 parts of  $\text{Ba}(\text{ClO}_4)_2$  (containing 2%  $\text{SiO}_2$  as the combustion "catalyzer").

#### Propellant 8

##### (a) Polyester-polyamide resin

20 parts of sebacic acid are heated under a reflux condenser for 15 hours in a nitrogen atmosphere with 20 parts of polyethylene glycol (mol. wt.  $\sim 400$ ), after which 40 parts of tetraethylene pentamine are gradually added. The reflux heating is continued and the water is distilled off. The viscosity of the product at  $18^\circ\text{C}$



is 44,500 cp.

(b) Epoxy resin -- triethylene glycol diglycidyl ether.

One part of each of the 2 resins is mixed with 2 parts of  $\text{NH}_4\text{ClO}_4$  (containing 1%  $\text{Fe}_2\text{O}_3$ ) [108].

## 8.2. Propellants with Thiokols

Mixtures which serve as initiators for solid rocket propellants.

Many recently developed propellants containing ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ), ammonium perchlorate ( $\text{NH}_4\text{ClO}_4$ ), asphalt, synthetic rubbers, etc. require a high ignition temperature and a high pressure to maintain combustion. For example, propellants with ammonium nitrate require  $\sim 300^\circ\text{C}$  and  $\sim 14$  atm, to initiate uniform combustion. In this case, the use of initiators becomes necessary.

The initiator fuel must be a mixture which is easily ignited and which furnishes a large amount of gaseous products during combustion. It is preferable if such a mixture is capable of generating gases for at least 500 milliseconds.

The following mixtures are used:

1. an oxidizer of  $\text{NH}_4\text{ClO}_4$  and  $\text{KClO}_4$
2. a polysulfide binder
3. well pulverized metals: Al, Mg and Ti.

It is most preferable if the oxidizer content is 60-75%, the metal content, 5-25% and the binder content, 10-40%. The oxidizer should be very finely pulverized: 0.05-0.15 mm (US sieve, 100-250), and the metals even more so: 0.04-0.05 mm (US sieve, 250-325).

Potassium perchlorate is the most desirable because its presence results in a high gas temperature. Other binding substances, such as neoprene, GR-S and copolymers of dienes with vinylpyridines can also be used instead of the polysulfides. However, the use of polysulfides assures easier casting and hardening at lower temperatures.

The polysulfides produced by Thiokol Chemical Corporation that are suitable for the above propellants are: LP-2, LP-3, LP-8, LP-32 and LP-33.

Combustible components with the following composition are particularly useful:

	parts by weight
diphenyl guanidine (accelerator)	0.5- 1.5
LP-3	7.5-37.5
p-quinone dioxime (vulcanizer)	1.0- 3.0
di(butoxyethoxyethoxy)methane (plasticizer)	0 - 3.0
sulfur (vulcanizer)	0 - 0.5
carbon black (filler)	1.0-10
MgO	0 - 0.5
Fe <sub>2</sub> O <sub>3</sub> (combustion catalyzer)	0 - 0.5

The compositions of some initiator mixtures are given in Table 8.1 [59].

TABLE 8.1. THE COMPOSITION OF SOME INITIATING MIXTURES CONTAINING THIOKOLS

Constituents	%					
LP-3	21.6	31.2	24.8	16.4	20.8	36.5
Diphenyl guanidine	0.6	0.9	0.7	0.5	0.6	1.1
p-Quinone dioxime	1.5	2.2	1.7	1.1	1.3	2.6
Di(butoxy-ethoxy-ethoxy)methane	1.1	1.6	1.2	0.8	1.0	1.8
Sulfur	0.1	0.2	0.1	0.1	0.1	0.4
Carbon black	2.2	3.1	2.5	1.6	0.5	3.6
MgO	0.2	0.3	0.2	0.2	0.2	0.4
Fe <sub>2</sub> O <sub>3</sub>	0.3	0.5	0.4	0.2	0.5	-
Al	7.1	5.9	16.4	10.7	6.0	3.6
NH <sub>4</sub> ClO <sub>4</sub>	-	19.7	52.0	-	-	-
KClO <sub>4</sub>	65.3	34.4	-	68.4	69.0	50.0

#### Rocket propellants with polysulfides

The thiokols, LP-2 and LP-3, are very convenient for solid propellant binders. They permit the formation of grains with large dimensions because they undergo



practically no volumetric changes during vulcanization; thus, no stresses develop in the charge.

Generally, polysulfide propellants (Table 8.2) [45] have the following composition:

	%	
oxidizer	50	-85
LP	15	-50
plasticizer	0	-20
vulcanizer	0.01-	5
accelerator	0	- 5

TABLE 8.2. THE COMPOSITION OF SOME ROCKET PROPELLANTS CONTAINING THIOKOLS

Constituents (in %)	Propellant number				
	1	2	3	4	5
KClO <sub>4</sub>	60.0	-	50.0	50.0	50.0
NH <sub>4</sub> ClO <sub>4</sub>	10.0	64.0	17.0	18.4	18.0
LP-2	19.5	25.7	23.0	30.4	-
LP-3	-	-	-	-	30.0
p-Quinone dioxime (vulcanizer)	-	-	0.5	0.6	2.0
PbO <sub>2</sub> (vulcanizer)	1.5	1.9	-	-	-
Dibutyl phthalate	1.5	-	-	-	-
Furfuryl alcohol (plasticizer)	7.2	8.0	7.51	-	-
Stearic acid	0.35	0.4	0.69	-	-
ZnO	-	-	1.3	0.6	-
Mixing temperature, °C	21-27	21-27	21-38	93	60

### 8.3. Propellants with Polyvinyl Chloride

The best combustible components based on polyvinyl chloride should contain about 50% plasticizer. The plasticizer must exhibit a high solubility of the polymer at elevated temperatures, and the colloidal solution thus obtained should have a low viscosity in order to be able to incorporate about 3 times as much oxidizer.

The universally known plasticizers of the sebacate, phthalate, adipate or glycol ester groups are employed. Dioctyl and dibutyl sebacates and dioctyl phthalate have proved to be the best. Plasticizers with the  $-\text{NO}_2$  or  $-\text{ONO}_2$  groups can be used only in mixtures with nonexplosive softeners.

The maximum amount of oxidizer that can be incorporated furnishes 90% of the oxygen required for transforming the combustible component into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . The following can be employed as oxidizers: ammonium, potassium and sodium perchlorates, ammonium and sodium nitrates and hexanitroethane, mannitol hexanitate, etc. Barium castorate in the amount of 1% serves as the stabilizer.

Sometimes, the copolymer of vinyl acetate with vinyl chloride, in which the vinyl chloride predominates percentagewise, is also used. An example of a propellant with polyvinyl chloride:

	parts by weight
polyvinyl chloride	50
barium castorate	2
dibutyl sebacate	50
$\text{NH}_4\text{ClO}_4$	306

The polyvinyl chloride is incorporated into the softener with the stabilizer. Then,  $\text{NH}_4\text{ClO}_4$  is added to the mixer. The mixture is cast into forms under a slight pressure and hardens for several minutes at a temperature of  $160-175^\circ\text{C}$ .

The hardened grain retains its elasticity down to about  $-50^\circ\text{C}$ . The burning rate is 0.25 cm/sec under atmospheric pressure and 1.27 cm/sec at  $140.6 \text{ kg/cm}^2$ . Other propellants of this type are described in Table 8.3 [37,99].

#### Propellants for small caliber rockets

A mixture of inorganic oxidizer with a thermoplastic combustible component, such as Vinylite VYNU (a high-molecular copolymer of vinyl chloride with a small amount of vinyl acetate) together with the plasticizer Cellosolve -- a neutral phosphoric ester of ethylene glycol monobutyl ether,  $\text{OP}(\text{OCH}_2\text{CH}_2\text{O C}_4\text{H}_9)_3$ , -- is used here.



TABLE 8.3. THE COMPOSITION OF 10 ROCKET PROPELLANTS CONTAINING POLYVINYL CHLORIDE

Propellant no.	Polymer	Z	Plasticizer	Z	NH <sub>4</sub> ClO <sub>4</sub> [%]
2	polyvinyl chloride	12	dioctyl sebacate	12	75
3	" "	12	dioctyl phthalate	12	75
4	" "	12	dibutyl sebacate	12	75
5	" "	12	{ dibutyl sebacate ester of acids with 6-10 carbon atoms and triethylene glycol	{ 8 4 }	75
6	" "	14.8	{ di(3,5,5-trimethyl-hexyl) adipate di(methoxy-ethyl) phthalate	{ 5.8 5.9 }	75
7	" "	19.5	{ di(3,5,5-trimethyl-bexyl) adipate di(methoxy-ethyl) pbthalate	{ 9.7 4.9 }	65.5
8	" "	18.3	di(3,5,5-trimethyl-bexyl) adipate	11	70.1
9	" "	14.8	{ di(3,5,5-trimethyl-hexyl) adipate di(methoxy-ethyl) phthalate	{ 5.9 5.9 }	73
10	" "	17.6	dibutyl sebacate	11.7	70.2
11	copolymer of 90% vinyl chloride and 10% vinyl acetate	18	di(3,5,5-trimetbyl-bexyl) adipate	18	63.5

The production method consists of 2 main stages:

- (a) Mixing of the finely pulverized constituents at room temperature.
- (b) Extrusion of the granules under a high pressure and at a higher temperature.

The temperature during extrusion must be selected so that the copolymer and plasticizer form a homogeneous physical mixture and that this mixture retains its thermoplastic properties. The granulated propellant can be (compression) molded into suitable shapes or inserted directly into the combustion chamber.

In order to assure good ignition and uniform combustion, the charge is formed of 3 parts: igniter, auxiliary charge and main charge.



The igniter consists of a mixture having a high combustion temperature:

958 g of titanium dust  
1385 g of  $\text{KClO}_4$

The auxiliary charge is for the purpose of generating a high pressure, which is indispensable for a stable combustion of the main charge. The composition of the auxiliary charge is as follows:

1736 g of  $\text{KClO}_4$   
742 g of aluminum dust  
222 g of titanium dust  
48 g of Vinylite VYNU  
72 g of Cellosolve

the mesh analysis of  $\text{KClO}_4$  in accordance with the US Standard Sieve

				mesh dimension in mm	%
on the sieve	50			0.297	0.1
" " "	70			0.210	2.7
" " "	100			0.149	26.8
" " "	140			0.105	30.8
" " "	200			0.074	31.2
through the sieve	200			0.074	8.7

The main charges:

Propellant 1

1754 g of  $\text{KClO}_4$ , dried at 100-110°C  
482 g of graphite dust  
222 g of titanium dust  
109 g of Vinylite VYNU  
163 g of Cellosolve

sieve mesh analysis of  $\text{KClO}_4$  in accordance with US Standard Sieve

		mesh dimension in mm	%
on the sieve	50	0.297	0.08
" " "	70	0.210	0.86
" " "	100	0.149	6.4
" " "	140	0.105	14.67
" " "	200	0.074	29.5
through the sieve	200	0.074	48.4

About 150 g of graphite are added to the perchlorate placed on sieve 70 and shaken. The through-screening breaks up the  $\text{KClO}_4$  agglomerates and the graphite protects against re-agglomeration by coating the oxidizer particles; the material that passes through the sieve and that which does not is mixed together.

The oxidizer, graphite, titanium and Vinylite are mixed together at a temperature of 10-30°C. The plasticizer Cellosolve, which can also be replaced by trioctyl phosphate, is added to this mixture and mixed for 10 minutes in a ball mill. Such propellants are stable for several months. The rubber-like properties are retained within the temperature range, -40 to +60°C. Other main charge compositions are given in Table 8.4 [50]. The screen analysis of  $\text{KClO}_4$  in propellants 2, 4, 5 and 6 is the same as in propellant 1. The screen analysis of  $\text{KClO}_4$  in propellant 3 is as follows:

		mesh dimension in mm	%
on the sieve US	100	0.149	49.7
" " " "	140	0.105	28.2
" " " "	200	0.074	17.8
through the sieve US	200	0.074	4.2

A propellant of composition: 12.5% polyvinyl chloride, 12.5% dibutyl sebacate and 75%  $\text{NH}_4\text{ClO}_4$ , and the effect resulting from the addition of chromites to it have already been discussed in section 7.2.1.



TABLE 8.4. THE COMPOSITION OF SEVERAL ROCKET PROPELLANTS CONTAINING VINYLITE VYNU

Constituents (in parts by weight)	Propellant number				
	2	3	4	5	6
KClO <sub>4</sub>	1156	2315	887	877	877
Al	594	989	463	62.3	83
Ti	148	296	-	27.6	-
Graphite	-	-	-	241	241
Vinylite VYNU	32	160	60	53.6	53.4
Cellosolve	48	240	90	80.4	80.0

#### 8.4. Propellants with Polyvinyl Acetate

Propellants for assisted launches,  
for rockets and as gas generators

These are propellants based on ammonium nitrate, because this oxidizer assures the evolution of a large amount of gases with a relatively low temperature. Thus the employment of these propellants in the activation of airplane engine air compressors or as a source of gases to convey the oxidizer and fuel into liquid-fuel rocket engines is possible.

The general composition of such propellants is as follows:

	%
NH <sub>4</sub> NO <sub>3</sub>	70 - 90
combustible component	10 - 25
organic dye	0.5 - 5
carbon black	0 - 5
inorganic "catalyzer"	0 - 4
modifier of exponent <u>n</u>	0 - 4
gassing inhibitor	0 - 4
surface-active agent	0 - 0.5

The combustible component is prepared by heating the plasticizer to  $\sim 150^{\circ}\text{C}$ , usually  $120-140^{\circ}\text{C}$ , and adding the polymer with simultaneous stirring until a homogeneous mixture is obtained. Then the modifier is added and later the ammonium nitrate with "catalyzers" (organic and inorganic). The oxidizer with "catalyzers" is mixed with the combustible component at a temperature below  $120^{\circ}\text{C}$  (it is better if it does not exceed  $110^{\circ}\text{C}$ ). Then it is cast or extruded into forms under a pressure of  $140-280 \text{ kg/cm}^2$ . The temperature of the gaseous combustion products ranges from  $800-1400^{\circ}\text{C}$ .

### Propellant 1

9.6 parts of 2,4-dinitro-diphenyl ether are heated at  $140^{\circ}\text{C}$  with 9.6 parts of ethylene glycol diglycolate. 5.8 parts of cellulose acetate (54-56%  $\text{CH}_3\text{COOH}$  after hydrolysis) are added and it is stirred until a homogeneous mixture is obtained. After the temperature has been lowered to  $110^{\circ}\text{C}$ , a mixture of 73 parts of ammonium nitrate with 2 parts of Prussian blue is added.

The burning rate is  $0.254 \text{ cm/sec}$  at  $70.3 \text{ kg/cm}^2$ ;  $n = 0.72$ .

By replacing 10% of the combustible component with Pyrogene Direct Blue RL-CL (color index, 956), a propellant of the following composition is formed:

	Z
cellulose acetate	5.18
2,4-dinitro-diphenyl ether	8.66
ethylene glycol diglycolate	8.66
Prussian blue	2.0
organic dye	2.5
$\text{NH}_4\text{NO}_3$	73.0

The burning rate is  $0.356 \text{ cm/sec}$  at  $70.3 \text{ kg/cm}^2$ ;  $n = 0.70$ . Other propellants of this group are given in Table 8.5.

The effect resulting from the addition of organic dyes on the burning rate of propellant 3 was discussed in section 7.2.1. [49].



TABLE 8.5. THE COMPOSITION OF SEVERAL ROCKET PROPELLANTS CONTAINING CELLULOSE ACETATE

Constituents (in %)	Propellant number			
	2	3	4	5
Cellulose acetate	4.6	5.8	6.6	4.8
Flexol 3GH (triethylene glycol dihexate)	-	-	-	3.6
Ethylene glycol diglycolate	7.70	9.6	5.7	-
2,4-dinitro-diphenyl ether	7.70	9.6	7.7	3.6
Pyrogene Direct Blue RL-CF	2.5	-	2.0	-
Prussian blue	3.0	2.0	-	-
Carbon black	1.0	-	2.0	3.0
NH <sub>4</sub> NO <sub>3</sub>	73.5	73.0	74.0	85.0
Burning rate $\bar{r}$ at 70.3 kg/cm <sup>2</sup> , in cm/aec	0.483	0.203	0.229	0.178
Exponent $\bar{n}$	0.70	0.68	0.74	0.68

### 8.5. Propellants with Methyl Methacrylate

#### Propellants with the consistency of mud

These are propellants in which methyl methacrylate dissolved in the plasticizer is subjected to polymerization before the oxidizer is added. Thus, the binder is a highly viscous liquid and, after mixing with the oxidizer, it forms a sort of thick putty or mud. It is true that propellants prepared in this manner do not have a large specific impulse, but they can readily be cast into the combustion chamber; and when ammonium nitrate is used as the oxidizer, they yield a large quantity of gaseous products. The latter is advantageous, e.g., in assisted launchers or in gas generators.

In order to reduce the oxygen deficiency, the following are used as plasticizers: nitrates of n-propyl, i-propyl, n-butyl, 2-methoxy-ethyl, nitro-n-propyl and



nitro-n-butyl. Several propellants of this type are given in Table 8.6.

TABLE 8.6. THE COMPOSITION OF SEVERAL ROCKET PROPELLANTS CONTAINING METHACRYLATES

Propellant number	Constituents	%	Remarks
1	$\text{NH}_4\text{NO}_3$ , US Sieve 180 (0.08 mm)	42.9	A slight separation of $\text{NH}_4\text{NO}_3$ was observed after 9 days. Specific impulse of 147 seconds at 35.15 kg/cm <sup>2</sup> .
	methyl methacrylate	14.4	
	2-methoxy-ethyl nitrate	42.7	
2	$\text{NH}_4\text{NO}_3$	51.0	A slight separation of $\text{NH}_4\text{NO}_3$ after 14 days
	methyl methacrylate	12.2	
	2-methoxy-ethyl nitrate	36.8	
3	$\text{NH}_4\text{NO}_3$	62.0	$\text{NH}_4\text{NO}_3$ does not separate after 90 days. Specific impulse of 179 seconds at 35.15 kg/cm <sup>2</sup> .
	2-ethoxy-ethyl methacrylate	11.5	
	2-methoxy-ethyl nitrate	26.5	

The methacrylate is added to the organic nitrate and heated at 40°C until the maximum viscosity is attained and then it is mixed with ammonium nitrate in a McRobert mixer [52].

A rather rare example of the employment of hydrazine nitrate as an oxidizer is the propellant of composition:

	%
hydrazine nitrate $\text{N}_2\text{H}_4 \cdot \text{HNO}_3$	60.00
methyl acrylate	25.60
allyl diglycol carbonate	3.60
methyl methacrylate	10.40
di-tertiary-butyl peroxide	0.40

in which the hardening of the propellant takes place in a form. The methyl acrylate is copolymerized with allyl diglycol carbonate and with methyl methacrylate under the influence of di-tertiary-butyl peroxide [92].

### 8.6. Propellants with Unsaturated Amides

As already stated in section 6.1.3, acrylamide monomers dissolve the inorganic salts of ammonium and amines to a rather substantial extent. As a result, several percent more of the oxidizer can be incorporated in the combustible component than would be the case if the monomer did not dissolve the oxidizer.

An example of the composition of such a propellant

	g
N,N-dimethyl acrylamide	22.94
$\text{NH}_4\text{NO}_3$	76.81
methyl ethyl ketone peroxide	0.25

Ammonium nitrate should have precise particle dimensions: 70% of 0.84-2.0 mm (US sieve, 10-20) and 30% less than 0.84 mm (US sieve, 20). This propellant is hardened at 43°C for 16 hours. The temperature of self-ignition is about 240°C; it does not explode when struck with a weight of 2 kg from a height of 100 cm.

The burning rate is:

	kg/cm <sup>2</sup>	cm/sec
at	35.15	0.127
"	70.3	0.145
"	105.4	0.168

$n = 0.26$ .

This propellant is stable within the temperature range: -54 to +74°C [54,92].

### 8.7. Propellants with Furfuryl Alcohol Derivatives

As already stated in section 6.1.4, the condensate resulting from the dehydration of furfuryl alcohol, commercially available under the trade name Duralon, is capable of polymerization under the action of strong acids, bases or acid salts, even in the presence of nitrocompounds. Consequently, in addition to such oxidizers as the perchlorates, nitrates, chromates, etc., high-energy organic substances such



as hexogen, pentaerythrite tetranitrate, tetranitrobutane (various isomers, e.g., 1,1,4,4-; 2,2,3,3-, etc.) can be used. However, when it is desirable to employ the above compounds in propellants, a deterrent must also be added. 2,2-dinitro propane, which is also a plasticizer, is an excellent deterrent.

The general composition of such propellants is as follows:

	%
oxidizer or high-energy organic compound	50-70
furfuryl resin	15-30
2,2-dinitro propane	15-30

The furfuryl resin (Duralon) is first mixed with 2,2-dinitro propane and then the finely pulverized oxidizer, or one of the high-energy organic compounds mentioned is added. The constituents are thoroughly mixed and, after the incorporation of one of the polymerization catalyzers ( $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{AlCl}_3$ ), it is cast into forms where the final hardening takes place. Several typical compositions of propellants with furfuryl resins are given in Table 8.7 [55].

TABLE 8.7. THE COMPOSITION OF SEVERAL ROCKET PROPELLANTS CONTAINING FURFURYL RESIN

Constituents (in %)	Propellant number				
	1	2	3	4	5
Duralon (furfuryl resin)	20.0	25.5	20.7	17.3	17.5
2,2-dinitro propane	20.0	19.6	16.0	18.0	18.2
Hexogen (cyclo-trimethylene-trinitro amine)	-	53	61.7	-	-
Pentaerythrite tetranitrate	60.0	-	-	-	-
$\text{NH}_4\text{NO}_3$	-	-	-	64.0	-
$\text{NH}_4\text{ClO}_4$	-	-	-	-	63.6
Inorganic acid (polymerization catalyzer)	-	1.9	1.6	0.7	0.7

### 8.8. Propellants with Diene Copolymers

Preparation of the copolymer Bd/MVP and propellants based on it

The most well known copolymers of this group and some of the best are the copolymers of 1,3-butadiene with vinyl derivatives of heterocyclic N-bases such as pyridine, quinoline and isoquinoline. The dienes are employed in amounts of at least 50% and the N-bases from 15 to 50%.

Propellants of this type generally have the following composition (however, not always in the given amounts):

		7
combustible component		10-25
	parts by weight	
copolymer Bd/MVP	100	
carbon black	10-30	
plasticizer	10-30	
silicon dioxide	0-20	
metallic oxide	0-5	
anti-oxidizer	0-5	
surface-active agent	0-2	
accelerator	0-2	
sulfur	0-2	
combustion "catalyzer"	0-30	
oxidizer		75-90

Copolymerization can take place in the mass or, as is often done, in an emulsion at 5°C.

An emulsion of this type has the following composition:

	parts by weight
1,3-butadiene	90
2-methyl-5-vinyl pyridine	10
water	200
potassium soap	6
potassium chloride	0.1



	parts by weight
sodium salt of alkylarylsulfonic acid	0.3
tetrasodium salt of ethylene-diamine-tetra-acetic acid	0.005
dodecyl tertiary mercaptan	0.6-0.8
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	0.2
$\text{K}_4\text{P}_2\text{O}_7$	0.253
para-menthane hydrogen peroxide	0.135
potassium dimethyl-dithio carbonate	0.15
phenyl- $\beta$ -naphthylamine	1.75

19.5 parts of carbon black to 100 parts of copolymer are added to the latex in order to initiate coagulation. Then another 2.5 parts of carbon black and 1.25 parts of flexamine are added. When separated from the aqueous layer, the mixture obtained is mixed in a ball mill with 20 parts of a di(butoxy-ethoxy-ethoxy)methane plasticizer and with 5 parts of MgO. Commercial ammonium nitrate, with a mean particle size of 40  $\mu$ , is thoroughly mixed with combustion "catalyzers" (picrates are not to be mixed with the oxidizer because of the possibility of an explosion!) and is added to the combustible component in a mill in an amount up to 83.5%. If one of the picrates is used for the combustible component, it is incorporated only after the combustible component has been mixed with the oxidizer. After a thorough mixing of the constituents, the propellant is subjected to shaping and hardening. The burning rate as well as the effect of picrates, styphnates, cupric chromite, ammonium chromate, copper dust and cupric oxide used as combustion "catalyzers" are discussed in section 7.2.1. [36].

Then we have a propellant with another composition, containing a quaternizing agent and a vulcanizer. From it it is possible to form a grain of large diameter, free from air holes, under high pressure [93].

	parts by weight
$\text{NH}_4\text{NO}_3$	75
copolymer 90/10 butadiene - 2-methyl-5-vinyl pyridine	21.91
carbon black	4.38



	parts by weight
benzylidene chloride	1.51
accelerator - Butyl-8	0.36
sulfur	0.31
ZnO	<u>0.91</u>
	104.38

#### Preparation of propellants with ammonium nitrate in phase III

As already stated in section 5.1.2, when heated to a temperature of 32°C, ammonium nitrate undergoes a phase transformation, in which its volume increases by about 3.8%. This is a disadvantageous effect because cracking may occur during combustion or storage of the grain due to internal stresses. In order to avoid this, a method of preparing the propellant above 32°C has been worked out. Above this temperature, the ammonium nitrate is in phase III and, after cooling, the propellant shrinks without generating stresses: it separates from the copolymer and does not completely fill the microspaces in the combustible component. After being heated above 32°C, it again assumes its former volume.

The ammonium nitrate is dried within the temperature range, 32 to 90°C, it is incorporated in the combustible component at 32-70°C and the mixture is hardened at 80-82°C.

Additives such as Milori blue and tricalcium phosphate not only change the ballistic properties of the propellant but also facilitate separation of the ammonium nitrate in phase IV from the combustible component.

A similar action is exhibited by finely crystalline waxes, petrolatum, etc.

The combustible component

	parts by weight
copolymer 90/10 1,3-butadiene/ 2-methyl-5-vinyl pyridine	100
carbon black	20
plasticizer TP-90B	20
accelerator SA-11.3	1
sulfur	0.75

	parts by weight
ZnO	3
stabilizer-flexamine	3
surface-active agent - Aerosol OT	1

Propellant composition (in parts by weight)	A	B
combustible component	17.5	17.5
NH <sub>4</sub> NO <sub>3</sub>	82.5	82.5
Milori blue	0.25	-
tricalcium phosphate	-	0.41
	100.25	100.41

The copolymer is dried in a Baker-Perkins mixer 12 and mixed with carbon black. The ammonium nitrate is subjected to drying in a Stokes rotary vacuum drier for 6 hours at a temperature of 93°C and cooled to a temperature of 32-71°C, after which it is mixed with Milori blue.

The copolymer is placed in a Banbury mixer and heated to 54°C. Then the remainder of the additives, except the plasticizer, are incorporated and it is mixed for about 2 minutes.

The oxidizer with the Milori blue must be incorporated in the first stage in an amount of 30% together with 30% of the plasticizer, and the remainder, gradually, in small portions. After intermixing for one minute, it is extruded into forms and hardened for 24 hours at 83°C

		A	B
The burning rate at 70.3 kg/cm <sup>2</sup>	cm/sec	0.262	0.262
The pressure exponent n [57]		0.57	0.60

The propellant with the following composition is obtained by a similar method:

	parts by weight
NH <sub>4</sub> NO <sub>3</sub>	81.05
Bd/MVP (90/10)	11.00



	parts by weight
di(butoxy-ethoxy-ethoxy)methane	2.21
carbon black	2.48
flexamine	0.33
MgO	0.49
Milori blue	<u>1.94</u>
	99.50

Flexamine and magnesium oxide are added during plasticization of the copolymer with the plasticizer at a temperature of 54-68°C. The oxidizer is added in 4 portions. Hardening takes place at 77°C for 18 hours [61].

The burning rate at 70.3 kg/cm <sup>2</sup>	cm/sec	0.376
Specific impulse	sec	188

#### Propellants with high-energy nitrogen compounds

With an oxygen deficiency in the propellant, which is almost always the case if the oxidizer is ammonium nitrate, the presence of carbon black results in the development of thick smoke. In order to prevent this, part or all the carbon black is replaced with compounds having a high nitrogen content, i.e., at least 30% N. These substances should exhibit 10% explosions at the most when 0.02 g of the compound is struck by a weight of 2 kg from a height of 15 cm (when investigating a liquid, disks of blotting paper, 1 cm in diameter, are soaked with it). Compounds such as the following are used: melamine, hexogen, cyclotetramethylene-tetranitroamine, ammonium picrate, ethylene-dinitro-amine, trotyl, dicyano-diamide, urea, hydrazine nitrate, etc., with a mean particle size of 0.03-50  $\mu$ , and preferably less than 10  $\mu$ .

The propellant is prepared in a Baker-Perkins, Bramley Beken or Bunbury mixer with horizontal or vertical paddles. The oxidizer is added in 4 lots. At the end, vacuum heating is used to remove any air inclusions.

If the nitrogen compound is very sensitive to shock, it is dissolved together with the combustible component and with the other additives in n-hexane, cyclohexane, benzene or acetone and only then is the oxidizer incorporated. During the

TABLE 8.8. THE COMPOSITION OF SEVERAL  
ROCKET PROPELLANTS CONTAINING MELAMINE

Constituents	Propellant					
	A		B		C	
	%	parts by wt. to 100 parts by wt. of copolymer	%	parts by wt. to 100 parts by wt. of copolymer	%	parts by wt. to 100 parts by wt. of copolymer
Copolymer Bd/MVP 90/10	9.96	100	9.96	100	9.96	100
Melamine	1.76	17.6	1.76	17.6	1.76	17.6
Plasticizer ZP-211	1.97	19.8	1.97	19.8	-	-
Plasticizer-triacetin	-	-	-	-	1.97	19.8
Flexamine	0.30	3.0	0.30	3.0	0.30	3.0
p-Quinone dioxime	0.21	2.1	0.21	2.1	0.21	2.1
MgO	0.50	5.0	0.50	5.0	0.50	5.0
ZnO	0.30	3.0	0.30	3.0	0.30	3.0
NH <sub>4</sub> NO <sub>3</sub>	85.00	852	81.40	816	81.40	816
NH <sub>4</sub> ClO <sub>4</sub>	-	-	3.60	36	3.60	36

mixing, the solvent is gradually driven off under reduced pressure. The grain is obtained by extrusion or casting under pressure. Hardening takes place at room temperature and, additionally, at a temperature of 21-121°C. The hardening time depends on the required properties of the propellant and ranges from 3 hours to 7 days. The composition of some propellants with melamine is given in Table 8.8. These propellants have a high burning rate, of the order of several cm/sec; this is specifically due to the high-energy nitrogen compound [88].

#### Propellants with silica gels

The effect of silicon dioxide on the burning rate was discussed in section 7.2.3. However, the main purpose of adding silica gel is to improve the physical properties of the propellant. Propellants having the composition given in Table 8.9 were hardened at 77°C for a week and for 2 weeks and then the maximum elongation,



tensile strength and modulus of elasticity were studied. Due to the greater tensile strength and modulus of elasticity, the propellant is able to bear much greater stresses; thus, it is more resistant to cracking than the same propellant without silica [3].

TABLE 8.9. THE EFFECT OF SILICA GEL ON THE PHYSICAL PROPERTIES OF PROPELLANTS CONTAINING THE COPOLYMER, Bd/MVP 90:10

Constituents (in parts by weight/ 100 parts by weight of copolymer)	Propellant no.		
	1	2	3
Bd/MVP 90/10	100	100	100
Carbon black	20	20	20
SiO <sub>2</sub> - mean particle size 32 $\mu$	0	1	3
NH <sub>4</sub> NO <sub>3</sub>	753	758	768
Di(butoxy-ethoxy-ethoxy)methane	20	20	20
Milori blue	18	18	18
ZnO	3	3	3
Flexamine	3	3	3
Aerosol OT	1	1	1
Sulfur	0.75	0.75	0.75
Accelerator SA-113	1	1	1
Tensile strength after 1 week of hardening (kg/cm <sup>2</sup> )	18.28	21.09	22.49
" " " 2 weeks " " "	23.20	30.93	29.52
Maximum elongation after 1 week of hardening (%)	11.0	16.7	13.2
" " " 2 weeks " " "	12.0	9.1	7.7
Modulus of elasticity after 1 week of hardening (kg/cm <sup>2</sup> )	210.9	203.9	330.4
" " " 2 weeks " " "	98.4	574.9	773.4

#### Propellants with a halogen polymer facilitating grain extrusion

Propellants with a high solids content in the form of oxidizer, combustion "catalyzer" and metallic elements were discussed in section 7.2.3. Most of these propellants are extruded under a tremendous pressure, ranging up to 1400 kg/cm<sup>2</sup>. Formidable difficulties are encountered when such a high pressure is used, and the



extrusion of many propellants would be practically impossible if highly halogenated polymers were not added.

The highly-halogenated polymer or copolymer is first mixed with the oxidizer in a ball mill or in a Banbury or Baker-Perkins mixer. Pulverized boron or other high-energy metal is added, together with the combustion "catalyzer", to the binder with plasticizer and only then is the oxidizer with polymer incorporated. The addition of metallic elements produces a significant increase in the specific impulse, which exceeds 200 seconds for such propellants.

Thus, e.g., a propellant with the following composition was prepared [103]:

	Z
combustible component	7
$\text{K}_2\text{NO}_3$	88
$(\text{NH}_4)_2\text{Cr}_2\text{O}_7$	0.5
polytrifluorochloroethylene	0.5
boron (0.8-1 $\mu$ )	2.0
magnesium (18-22 $\mu$ )	2.0

where the combustible component has the following composition:

	parts by weight
copolymer Bd/MVP 90/10	100
carbon black	22
flexamine	3
plasticizer - butarez-25 <sup>2)</sup>	48

This propellant is cast under a pressure of 560-703 kg/cm<sup>2</sup> into grains of dimension: 12.7 x 7.62 x 3.8 cm, which are burned in a small engine. The results of the studies (Table 8.10) indicate that the propellant remains stable for at least 6 months at 77°C and the durability at room temperature is several times greater [62].

<sup>2)</sup> See page 325

TABLE 8.10. THE EFFECT OF AGEING TIME ON THE BURNING RATE AND THE SPECIFIC IMPULSE OF A PROPELLANT CONTAINING THE COPOLYMER, Bd/MVP 90:10

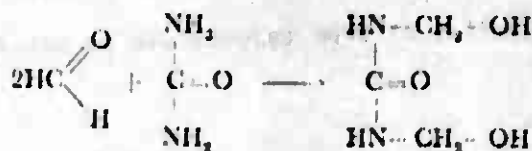
Ageing time (at 77°C)	Temp. [°C]	Burning rate $\bar{r}$		Specific impulse at 70.3 kg/cm <sup>2</sup> [sec]
		at 42.2 kg/cm <sup>2</sup> [cm/sec]	at 70.3 kg/cm <sup>2</sup> [cm/sec]	
Immediately after preparation	24	0.514	0.743	210
3 months	24	0.527	0.756	214
6 months	24	0.525	0.754	209

A propellant with binder based on the copolymer  
Bd/MVP, reinforced with aldehyde resins

Unhardened thermosetting resins, such as aldehyde polycondensates with phenols, urea or melamine, are added to the binder in order to improve the physical properties of propellants. The following aldehydes: formic, acetic, propionic, benzoic, etc., and phenols: phenol, o-, p- and m-cresol, xylenols, resorcinol, etc. are employed here.

0.75-3 moles of aldehyde to 1 mole of phenol are used in the phenol resins. Condensation takes place in an acidic or basic environment. Acidic condensation is employed if it is desirable to increase the mechanical strength; and basic condensation, if it is necessary to increase the thermal strength of the grain.

During the reaction of formaldehyde with urea, the first substance to evolve is dimethylol urea



which gives off water in a slightly acid environment and forms a resin which can be hardened at an elevated temperature.



In the reaction of melamine with formaldehyde, methylol derivatives first appear; these are then condensed to yield a thermosetting resin. 1-6 moles of formaldehyde to 1 mole of melamine are used. The resins discussed above are added in amounts of 10-60 parts to 100 parts of copolymer.

The combustible component generally has the composition:

	parts by weight
copolymer Bd/MVP	100
aldehyde resin	10- 60
plasticizer	0-200
surface-active agent	0- 10
anti-oxidizer	0- 3
vulcanization accelerator	0- 5
sulfur	0- 2
quaternizing agent	0- 25
metallic oxide	0- 5

There are 2 methods of preparing the propellant. In one method, the resin is incorporated into the copolymer heated to 77-88°C. The temperature must be lower than the temperature of hardening of the resin or copolymer. In the other method, the copolymer is ground in a cold mill and mixed while incorporating the resin. Only then is the temperature raised to 77-88°C. Then the remaining portions of the combustible component are added and subsequently the oxidizer with the combustion "catalyzer". A mixture prepared in this manner is cast under pressure or extruded and hardened at 21-116°C, either under atmospheric pressure or under an increased pressure.

The following is the composition of such a propellant:

	%
copolymer Bd/MVP 85/15	5.1
Schenectady Resin 6601 <sup>3)</sup>	2.2
flexamine	0.3

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<sup>3</sup>See page 325

butarez-25 (plasticizer) <sup>4</sup>	5.1
Philrich 5 (plasticizer) <sup>5</sup>	2.0
hexachloro-p-xylene (quaternizing agent)	0.3
cyanoguanidine	10.0
NH <sub>4</sub> NO <sub>3</sub>	75.0

This propellant has the burning rate:

at 35.15 kg/cm <sup>2</sup>	0.091 cm/sec
at 70.3 kg/cm <sup>2</sup>	0.147 cm/sec
exponent n	0.69

$\pi_p$ , the temperature sensitivity (coefficient) of the pressure, is 0.20%/°C.

The mechanical properties of this propellant are given in Table 8.11. Due to the very low burning rate, these propellants are suitable as gas generators [104].

TABLE 8.11. THE EFFECT OF THE HARDENING TIME ON THE MECHANICAL PROPERTIES OF A PROPELLANT CONTAINING THE COPOLYMER, Bd/MVP 35:15

Hardening (at 88°C)	Tensile strength $R_r$ [kg/cm <sup>2</sup> ]	Maximum elongation $\epsilon$ [%]	Modulus of elasticity $E$ [kg/cm <sup>2</sup> ]
24 hours	15.54	2.8	930.46
1 week	13.36	2.0	1167.1
2 weeks	15.88	3.0	2067.0

Binding substances for combining  
small charges into larger ones

The method of agglutinating small charges makes possible the obtaining of grains weighing more than 3000 kg. However, binding substances are not readily available because they must fulfil a number of conditions. They should be elastic

<sup>4,5</sup> See page 325



in order to resist inertial forces, mechanical shocks and thermal stresses, which tend to separate the individual components of the propellant. This condition entails a massive reduction in the amount of oxidizer (it causes brittleness). At the same time it is necessary that the binding substance have the same burning rate as the individual components of the charge.

Elements of the charge form concentric sectors of a ring, and the space between them is filled by the binding substance. It is used in the form of thin foils (0.025-0.25 cm) or in the form of a viscous liquid. Under an applied pressure, the fuel slugs are intimately bonded to the binding substance and then the whole mass is hardened at a temperature of 77-93°C.

The binding substance is prepared in the following manner. The oxidizer is dissolved in a polar solvent, e.g., in acetone, and mixed with a benzene solution of the copolymer. A coorecipitate of the copolymer with the oxidizer evolves in this mixture and is subsequently decanted and dried. Then, the vulcanizing agents, combustion "catalyzers", plasticizers, anti-oxidizers, vulcanization accelerators, etc. are added.

The oxidizers used here are perchlorates of sodium, potassium, magnesium and ammonium; chlorates of strontium and lithium; and nitrates of potassium, sodium, calcium and ammonium. The amount of oxidizer is 2-25%, preferably 5-15%. Oxidizer solutions in a polar solvent with from 30 to 100% saturation and solutions of rubbers in a nonpolar solvent of 8-10 g of copolymer in 100 g of solvent are used.

The burning rate is regulated by the amount of oxidizer, its type, particle size (from 1 to 300  $\mu$ ) and by the combustion "catalyzers" such as: cupric chromite ( $\text{CuO} \cdot \text{Cr}_2\text{O}_3$ ), ammonium dichromate, potassium dichromate, sodium dichromate, Prussian blue or Milori blue. The burning rate can be matched to requirements within the limits of 0.127-0.508 cm/sec at a pressure of 70.3 kg/cm<sup>2</sup>.

The general composition of the binding substance is as follows:

inorganic oxidizer ( $\text{NH}_4\text{ClO}_4$ )	2-25%, preferably 5-15%
rubber (Bd/MVP)	98-75%, preferably 95-85%



For example, a solution of 1.98 g of  $\text{NH}_4\text{ClO}_4$  in 180 ml of acetone at 25°C and, separately, a solution of 35 g of the copolymer Bd/MVP in 90 ml of benzene at 25°C are prepared. Then the 2 solutions are mixed. A coprecipitate is immediately formed, which is decanted and dried at 60°C. The  $\text{NH}_4\text{ClO}_4$  content in the coprecipitate is about 9%.

The above-described method of bonding the charge is not limited to propellants with the copolymer Bd/MVP. It can also be successfully used for propellants with binders based on other synthetic rubbers, such as the butadiene-styrene copolymer, Perbunan, butyl, neoprene, polybutadiene, acrylonitril-styrene, the thiokols, etc. [39].

Generally, these propellants predominantly contain:

combustible component	17.5%
oxidizer ( $\text{NH}_4\text{NO}_3$ , $\text{NH}_4\text{ClO}_4$ )	82.5%

In addition, about 1-2% of Milori blue is added.

Several combustible components used in the above-described propellants are given in Tables 8.12 and 8.13.

After being mixed with the oxidizer and combustion "catalyzer", the grain is extruded at a temperature of 82-88°C. The grain size that can be obtained by extrusion ranges from 15 to 30 kg. By employing the bonding method, a charge of about 3,000 kg can be prepared from 100 such elements. Then the whole mass is subjected to hardening at a temperature of about  $80 \pm 3^\circ\text{C}$  for 16-24 hours [64].

#### High-energy propellants with boron or other metals

Propellants with boron in their composition contain a very small amount of combustible component because the stoichiometric amount of oxygen required for oxidation of the combustible component and the boron is supplied by the oxidizer only when it is in the amount of about 90% of the propellant; moreover, the boron itself further increases the solid fraction content. Propellants with such a composition present formidable difficulties in extrusion of the grain, and extrusion may even

TABLE 8.12. SEVERAL COMBUSTIBLE COMPONENTS WITH THE COPOLYMER Bd/MVP 90:10 WHICH ARE SUITABLE FOR PROPELLANTS COMPOSED OF LARGE BONDED CHARGES

Constituents (in parts by weight)	Propellant no.		
	1	2	3
Copolymer Bd/MVP 90/10	100	100	100
Carbon black	60	20	40
Epichlorohydrin	-	8	-
Sulfur	-	2	1.75
ZnO	3	6	3
Flexamine	-	-	1.5
Wood resin	5	-	5
Dibutyl phthalate	50	-	5
Liquid polybutadiene	-	100	10
Accelerator butyl-8	-	-	3
$(\text{NH}_4)_2\text{CO}_3$	-	5	7.5
Chloranil	3	-	-

TABLE 8.13. A COMBUSTIBLE COMPONENT WITH THE COPOLYMER BUTADIENE-STYRENE 90:10 WHICH IS SUITABLE FOR PROPELLANTS COMPOSED OF LARGE BONDED CHARGES

Constituents	Parts by weight
Copolymer GR-S 1505 (90/10 butadiene-styrene)	100
Carbon black	50
ZnO	3
Sulfur	1.5
Flexamine	1.5
Stearic acid	1.5
Wood resin	5
Plasticizer - pentaryl A (amyl-diphenyl)	10
Accelerator - butyl-8	3.5



become impossible. There remains the compression molding method, which does not facilitate the obtaining of larger charges. The mechanical strength of such propellant is unsatisfactory.

Several methods have been worked out that permit the formation of charges with a high oxidizer content and with high-energy elements. One of these is based on grinding the high-energy element with the solid oxidizer and with a small amount of the combustible component and then forming small spheres, tablets or rods on appropriate presses. A propellant thus prepared is placed into a form and the liquid polymer with the oxidizer suspension is poured over it. Another method is based on mixing the propellant in tablet form with the oxidizer suspension in the polymer and then casting the whole mass into forms. The propellant obtained by both methods is subjected to hardening.

The high-energy elements used are beryllium, boron, lithium, aluminum, magnesium, silicon and titanium. They should be ground to an average particle size of about 20  $\mu$ . A mixture of 2 or 3 elements can be used and their content in globules should be 2-20%, preferably 5-10%.

The oxidizers can be:  $\text{NH}_4\text{NO}_3$ ,  $\text{NH}_4\text{ClO}_4$ , hexanitroethane, the ammonium salt of nitroform, hydroxylamine nitrate, hydrazine nitrate, etc. The amounts of oxidizer in the globules can be 80-95%.

The third constituent of the pellets, the binder, is polybutadiene, the copolymer Bd/MVP, the butadiene-styrene copolymer, alkyl cellulose with less than 6 carbon atoms in the alkyl group (e.g., ethyl cellulose), polytetrafluoro ethylene, etc.

If it is necessary to use a combustion "catalyzer", it should not exceed 5% of the pellet composition.

The formed pellets are 0.3-0.6 cm in diameter. Such pellets can be formed by machines designed to make pills or tablets, or it is also possible to extrude rods, which are then cut.

The amount of oxidizer suspension in the polymer depends on the packing of the pellets. It has been determined experimentally that the volume not occupied by the

pellets amounts to about 39.5%, but usually the volume of the suspension used is greater than 40%. If pellets with a different diameter are used, the porosity can be reduced to 15%, or even further. In the method of mixing with the oxidizer suspension in the binder, the individual pellets do not make contact with each other and, as a result, the volume not occupied by them increases to about 48%.

The liquid polymer used to pour over the pellets is selected from the group of polysulfides, liquid polybutadiene or the polyurethans. The oxidizer added to this polymer is  $\text{NH}_4\text{ClO}_4$ ,  $\text{KClO}_4$ ,  $\text{NH}_4\text{NO}_3$ , etc. The ratio of polymer to oxidizer is generally 50:50 to 20:80.

#### Propellant 1

##### (a) Pellet composition ( $\emptyset$ 0.48 cm)

	%
boron	8
ethyl cellulose	2
$\text{NH}_4\text{ClO}_4$	90

##### (b) Mixture of oxidizer with polymer

polyurethan	a	b	25%
	%	%	
castor oil	57.14	56.31	
neopentyl glycol	10.86	-	
toluene-diisocyanate	32.00	32.43	
hexylene glycol	-	11.26	
$\text{NH}_4\text{ClO}_4$			75%

This mixture is added to the form with the pellets in an amount of 40% of the finished product. It is hardened at 71°C for 48 hours. The specific impulse is 260 seconds.

#### Propellant 2

##### (a) Rod composition ( $\emptyset$ 0.6 cm and length 0.6 cm)



combustible component

10.5%

parts by weight

copolymer Bd/MVP 90/10	100
flexamine	3
plasticizer - liquid polybutadiene	25
plasticizer - light oil of the naphthene type (from petroleum)	25
p-quinone dioxime	2
$\text{NH}_4\text{ClO}_4$	84.5%
boron	5.0%

(b) The mixture of polymer with the oxidizer

combustible component

20%

%

castor oil	51.0
2-hydroxy-ethyl castorate	26.4
hexamethylene diisocyanate	22.6
$\text{NH}_4\text{ClO}_4$	80%

It is hardened at 71°C for 48 hours. The specific impulse is 247 seconds.

### Propellant 3

(a) pellet composition ( $\phi$  0.3 cm)

	%
polyisobutylene	2
combustible component from propellant 2a	3
$\text{NH}_4\text{ClO}_4$	77.5
decaborane	17.5

The pellets in the form are covered with the mixture from propellant 2b. The specific impulse is 263 seconds [40].

Propellants with decaboranes ( $\text{B}_{10}\text{H}_{14}$ )

Decaborane has a greater heating value per unit weight than boron, but because of its low specific gravity it has a relatively low heating value per unit volume.



However, it is considerably superior to boron with respect to ease of combustion. As is well known, during the burning of boron, the liquid and difficultly volatile  $B_2O_3$  flood the burning surface, cutting it off from the flame. This frequently results in the incomplete combustion of the boron. On the other hand, because decaborane has a low melting ( $99.7^\circ C$ ) and boiling ( $213^\circ C$ ) point, it is evolved in gaseous form during burning of the grain; obviously this eliminates the difficulties involved in the case of elemental boron.

Several propellants with decaborane and with the following combustible component are given in Table 8.14.

Organic combustible component

	parts by weight
copolymer 90/10 Bd/MVP	100
furnace black	20
tri(2-ethyl-hexyl) phosphate (plasticizer)	20
benzylidene chloride	6.6
sulfur	1.75
ZnO	5
vulcanization accelerator butyl-8	2
surface-active agent Aerosol-OT	1

It is evident from Table 8.14 that the addition of the first 5% of decaborane is the most effective. In that case the specific impulse increases by about 11%, while twice as much decaborane (a 10% addition) produces almost an identical increase in the specific impulse (by about 12%) with respect to the propellant without decaborane. Then, in spite of further addition of decaborane, the specific impulse value remains practically at the same level. The reason for this is the decreasing oxidizer content (due to the increased decaborane content) and the simultaneously increasing difference between the necessary stoichiometric active oxygen content in the propellant and the actual content. An increasingly larger portion of the organic combustible component remains unoxidized. The resulting loss of chemical energy counterbalances the larger heating value of the decaborane. Because only an

TABLE 8.14. THE EFFECT OF THE AMOUNT OF DECABORANE ON THE SPECIFIC IMPULSE OF A PROPELLANT WITH BINDER CONTAINING THE COPOLYMER Bd/MVP 90:10

Propellant	$\text{NH}_4\text{ClO}_4$ [%]	Organic combustible component [%]	$\text{B}_{10}\text{F}_{14}$ [%]	Specific impulse [sec]
1	90.0	5	5	262
1a	90.0	10	-	236
2	87.5	5	7.5	268
2a	87.5	12.5	-	241
3	85.0	5	10.0	270
3a	85.0	15	-	240
4	82.5	5	12.5	272
4a	82.5	17.5	-	235
5	80.0	5	15	274
5a	80.0	20.0	-	229
6	77.5	5	17.5	275

equalization occurs and not an increase in the chemical energy content of the propellant and because decaborane is a very expensive constituent, propellants containing smaller amounts of it are more advantageous [112].

#### 8.9. Propellants with Polyesters

Many polyester-styrene propellants were discussed in section 7.2 in connection with the effects of polychromates, lead salts, silicates, titanates and phosphates.

#### Bonding of polyester-styrene charges with the combustion chamber walls

The problem of preparing the bonding coating of the charge with the chamber wall is a very important, although difficult one. This layer or coating should assure the adhesion of the charge to the wall under various temperature conditions and

with different stresses. It is composed of materials such as glass fabric, metal fabric, cloth, etc., which are impregnated with polyester resins with the addition of an olefin monomer capable of producing a space lattice with the resin. The monomer is mixed with the liquid resin.

The grain is formed of polyester resin similar to the coating resin except that the resin of the grain is harder. This similarity of the resins is necessary for an intimate union of the grain with the coating layer after hardening. Several polyester resins that serve as binders are listed in Table 8.15.

TABLE 8.15. THE COMPOSITION OF SEVERAL POLYESTER RESINS SUITABLE AS BINDERS FOR SOLID ROCKET PROPELLANTS

Constituents (in moles)	Propellant							
	A	B	C	D	E	F	G	H
Sebacic acid	4	-	-	-	-	-	-	-
Adipic acid	-	7	7	0.9	0.9	0.8	0.9	0.8
Maleic anhydride	1	3	3	0.1	0.1	0.2	0.1	0.2
Ethylene glycol	-	11	-	-	-	-	-	-
Diethylene glycol	-	-	12	1	-	-	-	-
Polyethylene glycol (mol. wt. 300)	-	-	-	-	-	-	1	1
Propylene glycol	5	-	-	-	-	-	-	-
Polypropylene glycol (mol. wt. 425)	-	-	-	-	1	1	-	-

The following resin with composition given in moles is suitable for uniting the coating layer with propellants based on binders:

fumaric acid	3.4
phthalic anhydride	2
ethylene glycol	3.6
diethylene glycol	3

A polyester of this type tends to harden at room temperature. In order to avoid this, it is necessary to add hydroquinone.



The addition of styrenes to the condensation products of the above constituents contributes to the heteropolymerization of the resin, after which the resin acquires thermosetting properties. Of course, other unsaturated compounds are also used, although not as universally as styrene, because the latter has the advantage of low cost in comparison, e.g., with acrylic acid esters, acrylonitrile, etc.

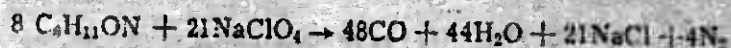
Conventional oxidizers in amounts of 45-90% are used in the polyester-styrene propellants. Cyclohexanol 1-hydrogen peroxide and cumene hydrogen peroxide, which are capable of inducing polymerization at room temperature, stand out among the heteropolymerization catalyzers. Organic cobalt salts (cobalt naphthenate, etc.) are polymerization accelerators. In addition to the conventional plasticizers, benzyl alcohol, which effectively counteracts brittleness in the propellant, has proved to be one of the best plasticizers [68,69].

#### 8.10. Propellants with Polylactams

##### Polylactam propellants with sodium and potassium perchlorate

Lactams with a 5-7 member ring, e.g., pyrrolidone, piperidone,  $\epsilon$ -caprolactam, are advantageous in that they readily polymerize even in the presence of large amounts of oxidizer. Alkali metals and alkaline-earth metals and their hydrides, borohydrides, oxides, hydroxides, carbonates, amides, etc. are polymerization catalyzers. The hydrides of sodium and lithium are especially useful. These catalyzers are added in amounts of 0.05-5%, preferably 0.1-1%, with respect to the lactam. In addition, initiators of the N,N-diacyl compound group, amine derivatives, etc., described in detail in section 6.1.9, are indispensable for polymerization. The polymerization process proceeds at temperatures up to 250°C, preferably at 130-170°C. The lower the molecular weight of the lactam, the lower is the required polymerization temperature.

The ratio of oxidizer to lactam ranges from 2.5:1 to 3.5:1. This ratio should be 2.84:1 for sodium perchlorate and  $\epsilon$ -caprolactam so that the reaction can proceed according to the summary equation:



For potassium perchlorate this ratio is 3.2:1.

Other constituents that increase the specific impulse are pulverized metals such as beryllium, boron, magnesium, aluminum; hydrides such as  $\text{MgH}_2$ ,  $\text{AlH}_3$ , borohydrides,  $\text{Al}(\text{BH}_4)_3$ , etc. These additives should be ground to a mean particle size less than 150  $\mu$ , preferably less than 74  $\mu$ , and they should not exceed 25% of the propellant; it is better if they are present in amounts of 5-10%.

Sulfamides, such as N-ethyl-p-toluene sulfamide, N-ethyl-o-toluene sulfamide; bi-substituted amides, such as dimethyl formamide; glycol ethers, such as ethylene glycol dimethyl ether, etc., are good plasticizers of the polylactams. They are used in amounts up to 35%, preferably 15-25% with respect to the lactam.

#### Propellant 1

One part of  $\epsilon$ -caprolactam with 0.01 parts of NaH and 0.5 mole percent of N-acetyl-caprolactam are heated to 160°C and 3 parts of  $\text{KClO}_4$  are incorporated. Polymerization proceeds very rapidly; the mixture solidifies in 10 minutes. It burns with a vivid, bright flame.

#### Propellant 2

One part of  $\epsilon$ -caprolactam, 0.05 parts of NaH and 1 mole percent of N-acetyl-caprolactam are poured into a container at 80°C. Then 3.2 parts of  $\text{KClO}_4$  are incorporated and the mixture is heated to 160°C until it solidifies.

#### Propellant 3

One part of  $\epsilon$ -caprolactam and 0.05 parts of NaH are heated to 160°C and placed in a vessel. One mole percent of N-acetyl-caprolactam is added and mixed well, then 2.84 parts of  $\text{NaClO}_4$ . It is heated at 160°C for about one-half hour [75].



### 8.11. Nitrated Hydroxypolymers

As already mentioned in section 6.1.11, polymers with double bonds can be hydroxylated with hydrogen peroxide in the presence of formic acid. After esterification with nitric acid, the hydroxypolymers obtained form inflammable substances with a high nitrogen content and are suitable as constituents for composite propellants.

#### Nitration of the hydroxypolymer

5 g of liquid hydroxypolybutadiene with mol. wt. of 850 and having 26% hydroxylated double bonds are dissolved in 30 ml of acetic anhydride. This solution is slowly added during a 45-minute period to a mixture of 30 ml of fuming  $\text{HNO}_3$  with 30 ml of acetic anhydride. The entire mass is cooled to about  $0^\circ\text{C}$  and mixed for 30 minutes. The temperature should not rise above  $5^\circ\text{C}$ . The mixture obtained is poured into 400 ml of water with ice, the precipitated polymer is drained, washed free of acid with water and dried. The finished product (8.5 g) is a yellow, finely powdered, inflammable substance with an 11% N content [41].

Footnotes

1. to p. 286. The propellant compositions are given in parts by weight.
2. to p. 309. A liquid polymer of butadiene.
3. to p. 311. The unhardened phenol-formaldehyde resin is manufactured by Schenectady Varnish Company, Schenectady, New York.
4. to p. 312. A liquid polybutadiene.
5. to p. 312. A highly aromatic, heavy residual petroleum produced by Philips Petroleum Company.



## 9. PROPELLANTS WITH DERIVATIVES OF NATURAL SUBSTANCES AND RARELY USED PROPELLANTS

### 9.1. Nitrocellulose Propellants

#### Propellants with the plateau effect

It has been determined that a small addition of lead salts (ous) to nitrocellulose propellants causes the plateau effect to appear. This is a very advantageous effect because it permits the utilization of powders of this type as propellants for rockets or guided missiles. It then becomes unnecessary to fear variations in the mass output or, even more important, explosions within a given pressure range. The effects of the different lead salts on the  $n$  exponent are discussed in section 7.3.

In addition to nitrocellulose, nitrocellulose propellants, termed colloidal propellants, contain plasticizers, which are explosive compounds such as nitroglycerin, nitroglycol, etc. Mixtures of explosive plasticizers with nonexplosive, universally used phthalates, sebacates, etc. are also used. Without lead salts these propellants are not suitable as rocket charges because they have the characteristic of unstable combustion in a closed space. The burning rate rapidly increases with increasing pressure and temperature, which leads to destruction (blow-out) of the container.

The general composition of this type of propellants, that are suitable for rocket propulsion, is as follows:

	%
nitrocellulose	40 - 70
plasticizer (explosive + nonexplosive)	4 - 45
lead salts	0.5 - 5
stab'lizer	0.5 - 2.5

The typical composition of such propellants [6]:

	%
nitrocellulose	58

	g
nitroglycerin	25
triacetin	9
dioctyl phthalate	3
plumbous cyclohexyloxy acetate	3.5
2-nitro diphenylamine	1.5

#### Method of uniform incorporation of additives into nitrocellulose fuels

In this method 2 solvents which are mutually miscible only to a slight degree are used. Most frequently, they are water and ethyl acetate. A nitrocellulose suspension is prepared in the water; and a suspension of other additives, such as carbon black, modifiers of the exponent  $n$  or "catalyzers", or the various additive substances are dissolved in the ethyl acetate. The 2 suspensions are energetically mixed until an emulsion is formed and colloid protectors, such as dextrine, amidon, gum arabic or animal protein, are added to increase the stability. During mixing, the nitrocellulose gradually dissolves in the ethyl acetate. By means of an appropriate mixing force and by the addition of various emulsifying agents, such as salts of fatty acids or sulfonated oils, it is possible to regulate the particle size of the emulsion. Then the temperature is raised to somewhat below the boiling point of water ( $99^{\circ}\text{C}$ ), the ethyl acetate evaporates off and the finished product precipitates out of the mixture. Before evaporation, a sodium sulfate solution, which reduces the amount of water in the particles of the emulsion through the osmotic effect, is added. The propellant thus obtained exhibits a lowered porosity.

In the method described, substances such as: carbon black, powdered aluminum, hexogen, calcium carbonate (stabilizer), powdered iron, iron oxides, minium, plumbous stearate, plumbous chromate, plumbous sulfide, plumbous azide, dyes, etc., can be incorporated.

The propellant thus obtained usually contains a small amount of plasticizer in order to maintain a constant consistency during precipitation from the aqueous suspension. After drying, this propellant is mixed with the plasticizer (which is

usually nitroglycerin with one of the nonexplosive plasticizers) and cast into forms. The forms with the propellant are raised to a temperature of 50-90°C until the mixture becomes homogeneous and sets. A grain prepared in this manner is highly homogeneous, and its strength and other mechanical and physical properties are adequate for rocket propulsion.

#### Propellant 1<sup>1)</sup>

(a) 250 parts of well pulverized nitrocellulose (12.6% N) are mixed with 4,100 parts of water at 50°C. A suspension of 0.7 parts of carbon black in 100 parts of ethyl acetate is prepared separately. This suspension is added to another 1,250 parts of ethyl acetate. Another 31.4 parts of dinitro toluene and 2.8 parts of ethyl centralite is added to this. Both of these suspensions are mixed together and the temperature is raised to 68°C. The mixing is continued for about one hour until the nitrocellulose dissolves in the ethylacetate. Then 25 parts of colloid protector (a type of animal protein) in 150 parts of water are added. In order to reduce the particle size of the emulsion, 24 parts of a 40% solution of sodium 2-ethylhexyl-sulfate are used. The desired particle size in the emulsion is 0.127 mm, preferably 0.025 mm. A solution of 155 parts of  $\text{Na}_2\text{SO}_4$  in 300 parts of water is incorporated over a period of one hour, and it is stirred for another 3 hours. Then the temperature is raised to 99°C, the ethyl acetate evaporates and the emulsified particles solidify. The finished product is drained and dried at 50°C. It contains:

87.7% nitrocellulose

11.0% dinitro toluene

0.3% carbon black

1.0% centralite

(b) about 56.18 parts of the substance thus prepared are placed in a Sigma paddle mixer and mixed for 16 hours under a vacuum of 10 mm Hg.

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<sup>1</sup>See page 345



In the meantime 37 parts of a plasticizer of composition:

74% nitroglycerin  
25% dimethyl phthalate  
1% ethyl centralite

are placed under a vacuum of 10 mm Hg and also allowed to remain for 16 hours. The 2 substances are mixed together under a vacuum in order to prevent air inclusions. After mixing, they are poured into forms with substances that are resistant to nitroglycerin, such as cellulose acetate, methyl methacrylate or ethyl cellulose. The forms with the mixture are heated to 75°C and this temperature is maintained until the propellant is dissolved and sets. Such a mixture sets in 21 hours if it remains at a low temperature of about 22°C.

#### Propellant 2

A mixture is prepared as in the case of propellant 1a. 5 parts of such a substance are allowed to remain in a mixer for 16 hours under a vacuum of 10 mm Hg. Separately, 10 parts of a plasticizer with a composition as in the case of propellant 1b are placed under a vacuum. The 2 substances are mixed under vacuum and 15 parts of  $\text{NH}_4\text{ClO}_4$  with a mean particle size of 0.0051 cm are added. Dissolution of the propellant in a plasticizer (from several minutes to several hours) and gelatinization take place in a heated screw pump or other at a temperature of 75-120°C. Then the finished propellant is extruded and cut.

#### Propellant 3

5 parts of a mixture as in the case of propellant 1a are stirred under vacuum of 10 mm Hg for 72 hours. At the same time, 10 parts of a plasticizer of composition:

49.5% nitroglycerin  
49.5% glycerin triacetate  
1.0% 2-nitro diphenylamine

are subjected to stirring under vacuum.

The 2 substances are mixed together with the addition of 15 parts of  $\text{NH}_4\text{ClO}_4$ . A dispersion is formed, which can be readily cast into forms. The forms are heated at  $75^\circ\text{C}$  until the propellant dissolves and sets.

Propellants with an ammonium perchlorate dispersion have a high burning rate [77, 78, 79].

#### A method of eliminating thermal stresses during grain preparation

In this method a mixture of oxidizer with resin (7:3) and with or without plasticizer is hardened and ground to a particle size of about  $1/2$  mm. The ground mixture is screened and placed in forms while being compressed under a slight pressure. In order to improve the packing, different particle sizes are used. A plasticizer, which causes the hardened particles to swell, is added to the forms with the pulverized substance. Diffusion of the plasticizer proceeds until a homogeneous mass is obtained. There are practically no thermal transformations during this process.

Ammonium perchlorate is used as the oxidizer and nitrocellulose or polyvinyl nitrate as the binder. Explosive or nonexplosive substances, such as 2,2-dinitro propane or triacetin, are used as plasticizers.

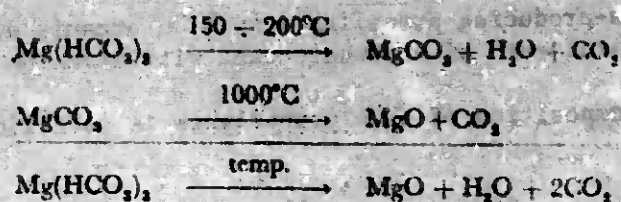
The oxidizer and the resin are chosen in a ratio of 70:30. When larger additive amounts are employed in order to improve particle bonding, a plasticizer with a monomer such as methyl methacrylate is added to the mold.

Because the universally used nitrocellulose with a 12.6% N content has a certain number of free  $-\text{OH}$  groups, it can be provided with a space lattice, that is, hardened, by means of these groups. The diisocyanates, which are added in amounts of 1-15% with respect to the nitrocellulose, are useful for this purpose. The less lattice formation agent, the slower the hardening will be, but it will be that much easier to control [53,105].

#### Nitrocellulose propellants with magnesium acid carbonate

In propellants of this type the magnesium acid carbonate serves as the deter-

rent and as a source of large amounts of gases. It decomposes in accordance with the following scheme:



The other principal constituents of these propellants are ammonium nitrate, nitrocellulose and a powdered, high-energy metal. Several examples of such propellants are given in Table 9.1.

TABLE 9.1. SEVERAL EXAMPLES OF NITROCELLULOSE PROPELLANTS WITH INORGANIC OXIDIZERS

Constituents (in %)	Propellant		
	A	B	C
$\text{NH}_4\text{NO}_3$	35	40	40
$\text{Mg}(\text{HCO}_3)_2$ (74 $\mu$ )	35	30	25
Nitrocellulose	20	20	25
Magnesium, aluminum or zinc (10-50 $\mu$ )	10	8	10
Aluminum soap (aluminum stearate)	-	2	-

The constituents are compression molded under a pressure of  $140.6 \text{ kg/cm}^2$ . If the  $\text{NH}_4\text{NO}_3$  content is increased to 50%, the mixture becomes explosive. Aluminum soap serves as the catalyzer, which facilitates the oxidation reaction of the metal; it is added in amounts of 0.1-2% of the propellant.

Propellants prepared in accordance with the above compositions have a very high combustion temperature, approximately  $4000^\circ\text{C}$  or even higher [79].

## 9.2. Propellants with Cellulose Acetate

Several propellants of this group have already been discussed in connection



with the action of organic stabilizers, surface-active agents and organic dyes in sections 7.1.2, 7.1.3 and 7.2.1.

Gas-producing propellants with an organic dye as the "catalyzer" of combustion and with ammonium nitrate

The general composition of such propellants is as follows:

	%
$\text{NH}_4\text{NO}_3$	70 — 90
combustible component	10 — 25
blue organic dye	0.5 — 5
carbon black	0 — 5
inorganic "catalyzer"	0 — 4
modifier of the exponent n	0 — 4
gas-acting inhibitor	0 — 4
surface-active agents	0 — 0.5

Because ammonium nitrate is used as the oxidizer, such propellants exhibit a slight corrosion tendency and generate large amounts of gaseous products; consequently, they are used as gas generators.

The combustible component is prepared by heating the plasticizer to a temperature of about 150°C and then mixing with the binding substance until a homogeneous mixture is obtained. Then the modifier of the exponent n is added, and later, at a temperature of about 120°C, the oxidizer with the combustion "catalyzers". The finished propellant is extruded or cast under a pressure of 140-280 kg/cm<sup>2</sup>. The combustion temperature is relatively low, about 800-1400°C. The following is an example of such a propellant:

9.6 parts of 2,4-dinitro-diphenyl ether with 9.6 parts of ethylene glycol diglycolate (obtained by the condensation of 1.2 moles of ethylene glycol with 1 mole of glycolic acid) are heated to 140°C and 5.8 parts of cellulose acetate (54-56%  $\text{CH}_3\text{COOH}$ ) are added. After a homogeneous mixture has been obtained, the temperature is lowered to 110°C and 73 parts of ammonium nitrate with 2 parts of Prussian blue are incorporated. When organic dyes are used, 10% of the combustible component is

replaced with them. The finished propellant is extruded or cast under pressure. The burning rate is 0.252 cm/sec at 70 kg/cm<sup>2</sup> and the exponent n equals 0.72. After replacement of 10% of the combustible component with Pyrogene Direct Blue RL-CL, the burning rate is 0.353 cm/sec at 70 kg/cm<sup>2</sup> and the exponent n equals 70 [49].

#### Gas-generating propellants with ammonium nitrate and with oximes

As can be seen in section 7.3, oximes have a radical action with respect to lowering the exponent n value. They are added in amounts of about 10% of the combustible component.

The combustible component:

	%
2,4-dinitro-diphenyl ether	34.64
ethylene glycol diglycolate	34.64
cellulose acetate (54-56% CH <sub>3</sub> COOH)	20.72
acetonylacetone dioxime	10.0

constitutes 23% of the propellant.

The oxidizer, which is ammonium nitrate, is divided into 2 portions. 70% is ground in a micro-mill at 14,000 rpm down to a particle size of 44  $\mu$ . The remaining 30% should have a particle size of about 0.5 mm. The 2 fractions are mixed together.

The binder with plasticizers and oxime are mixed at 110-120°C and one third of the ammonium nitrate, mixed with Prussian blue and carbon black, is added rapidly. After 15-20 minutes of mixing, the remaining two thirds of the ammonium nitrate is incorporated. This is mixed for another 30-40 minutes, 15 minutes of which is under a vacuum of at least 330 mm Hg.

A propellant prepared thus has the following composition:

	%
cellulose acetate	4.70
2,4-dinitro-diphenyl ether	8.00
ethylene glycol diglycolate	8.00
insoluble Prussian blue	3.00
acetonylacetone dioxime	2.3



	%
$\text{NH}_4\text{NO}_3$	73.0
carbon black	1.0

This propellant flows freely at 100°C and is solid at temperatures below 90°C; it tolerates 2 cycles of heating for 2 hours at 80°C and cooling for 2 hours at -60°C [1].

#### Shielded gas-generating propellants

The shielding substances can be asphalt, asbestos, cellophane, cellulose acetate, etc. However, it is better if these substances have a composition similar to the main charge.

Two basic shielding methods are employed. In one method, a liquid, but highly viscous substance is sprayed on the surface of the grain. In the other method, the form or mold is lined with a foil of the coating material and, after the charge has been poured in, it is subjected to the action of pressure and temperature. The thickness of the coating is 2-10 mm in both cases.

For propellants with cellulose acetate or cellulose acetate butyrate, the best shielding substance is cellulose acetate (54-56%  $\text{CH}_3\text{COOH}$ ) in an amount of 40-60% with the plasticizer in the amount of 40-60%. The mixture containing the 2 substances is heated at 130-150°C under a pressure of 580 mm Hg until complete plastification is achieved (2-3 hours).

#### Principal charge

6.5 g of dry cellulose acetate, and then 7.8 g of triethyl acetyl citrate, 6.8 g of 2,4-dinitro-phenoxy ethanol, 1.7 g of asphalt, 3 g of sodium barbiturate, 3 g of gas black and 1 g of 2,4-diamine toluene are added to 70.2 g of ammonium nitrate (dried at 120°C for 1 hour under reduced pressure). This is mixed at 110°C under 580 mm Hg for 1 hour and 15 minutes.

### Shielding substances

(a) Cellulose acetate (54-56%  $\text{CH}_3\text{COOH}$ ) is mixed with triethyl acetyl citrate in a ratio of 1:1 and heated at  $140^\circ\text{C}$  under 580 mm Hg for 2 hours.

(b) 40% cellulose acetate with 60% triethyl acetyl citrate. After lining the mold with a foil of the above composition, the principal charge is poured in and allowed to react at  $110^\circ\text{C}$  under a pressure of  $232 \text{ kg/cm}^2$  for 10 minutes. This coating does not separate when the charge is held at  $77^\circ\text{C}$  for 30 days.

(c) 60% cellulose acetate with 40% triethyl acetyl citrate are mixed at  $150^\circ\text{C}$  under 580 mm Hg for 3 hours. 60% is the maximum permissible amount of cellulose acetate. With larger amounts, difficulties arise in extrusion or squeezing out of the foil.

Substances containing 30 or 35% cellulose acetate and 70 or 65% plasticizer do not have satisfactory properties. During heat tests they separate from the charge [81].

Propellants with cellulose acetate or other cellulose esters and with ammonium perchlorates

The particles of cellulose esters used for propellants should be spherical and have a diameter of 100  $\mu$ , 50  $\mu$  and 20  $\mu$ . With a particle size of 100  $\mu$ , the plasticizer must contain at least some of a self-oxidizing compound. Cellulose esters

TABLE 9.2. SOME EXAMPLES OF PROPELLANTS WITH CELLULOSE ESTERS

Propellant number	Constituents	%	Remarks
1	Cellulose acetate $\phi$ 1-15 $\mu$	10	The constituents are mixed and poured into molds. Setting (solidification) at $140-145^\circ\text{C}$ for 20 minutes
	Diocetyl phthalate	15	
	$\text{NH}_4\text{ClO}_4$	75	
2	Cellulose acetate	10	Setting at $140-145^\circ\text{C}$ for 15 minutes.
	Glycerin triacetate	15	
	$\text{NH}_4\text{ClO}_4$	75	

TABLE 9.2. (continued)

Propellant number	Constituents	%	Remarks
3	Cellulose acetate Ø 25 µ	12	Setting at 150-155°C for 5 minutes.
	Diethyl phthalate	18	
	NH <sub>4</sub> ClO <sub>4</sub>	70	
4	Cellulose acetate-sorbate Ø 25 µ	10	Setting at 104°C for 1 hour
	Diethyl phthalate	15	
	NH <sub>4</sub> ClO <sub>4</sub>	75	
5	Cellulose acetate-sorbate Ø 25 µ	12	Setting at 104°C for 1 hour
	Diethyl phthalate	18	
	NH <sub>4</sub> ClO <sub>4</sub>	70	

TABLE 9.3. SOME EXAMPLES OF PROPELLANTS WITH CELLULOSE ACETATE

Propellant number	Cellulose acetate [%]	Softener	%	NH <sub>4</sub> ClO <sub>4</sub> [%]
1	12	Triethylene glycol diacetate	9 }	70
		Diethyl phthalate	9 }	
2	10	Diethyl phthalate	15	75
3	18	Diethyl phthalate	13.5 }	55
		Nitroglycerin	13.5 }	
4	16	Diethyl phthalate	12 }	60
		Nitroglycerin	12 }	
5	10	Diethyl phthalate	10 }	70
		Nitroglycerin	10 }	
6	13.3	Diethyl phthalate	10.7 }	60
		Nitroglycerin	16 }	

with a particle size greater than 50 µ can be used for propellants with inactive plasticizers. The best temperature for mixing the constituents is 35°C. When

nitroglycerin is employed, the mixing temperature cannot exceed 115-120°C. Propellants of this type are given in Tables 9.2 and 9.3 [38].

#### Gas-generating propellants with sodium anthranilate

Propellants of this type (Table 9.4) are particularly suitable as gas generators because they have a low burning rate, liberate large volumes of gas, and yield gaseous products which do not corrode the nozzle. Sodium anthranilate serves as a

TABLE 9.4. THE COMPOSITION OF SOME PROPELLANTS WITH SODIUM ANTHRANYLATE

Constituents (in %)	Propellant no.		
	1	2	3
Cellulose acetate (Lakierniczy* - 55% CH <sub>3</sub> COOH)	8	12	11
Plasticizer mixture**	7	9	9.5
Triethyl acetyl citrate	7	9	-
Triacetin	-	-	9.5
Carbon black	3	4	4
Toluene diamine	1	1	1
NH <sub>4</sub> NO <sub>3</sub>	71	62	62
Sodium anthranilate	3	3	3
Burning rate r (cm/sec)	0.203	0.203	0.178
Pressure exponent n	0.45		

\*Translator's note: Unable to find meaning

\*\*2 parts by weight of dinitro-phenoxy ethanol + 1 part by weight of di(dinitro-phenoxy) ethane

combustion "catalyzer". A solution of cellulose acetate in plasticizers is prepared at 130°C. After cooling to 100°C, the ammonium nitrate, carbon black and amine are incorporated. The sodium anthranilate is incorporated only when the formed mixture has the consistency of a paste, and the propellant is subsequently extruded or cast into molds [113].

### 9.3. Propellants with Asphalts and Pitches

Some propellants with pitch and with asphalt were discussed in section 6.1.12.

#### Propellants with asphalt and ammonium nitrate thickeners

Numerous examples of thickeners and their effect on the burning rate and combustion stability of propellants with asphalt and with ammonium nitrate were discussed in section 7.2.4. This effect also depends on the method used to incorporate the thickener. The only effective method is "wet" mixing, in which the thickener is incorporated into a 50% aqueous solution of ammonium nitrate with subsequent evaporation. Some propellants with thickeners are given in Table 9.5 [44].

#### Propellants with asphalt and with the styrene-acrylonitrile polymer

The styrene-acrylonitrile polymer is added in order to improve the properties of propellants based on asphalt. The 2 substances are employed in ratios of 7:3 to 1:9, i.e., asphalt 10-70% and the styrene-acrylonitrile polymer, 30-90%. Binders with the above compositions make up 30-60% of the combustible component. The remainder is made up by the plasticizer.

Generally, propellants of this type have the following composition:

	%
$\text{NH}_4\text{NO}_3$	65-90
combustible component	8-25
combustion "catalyzer"	1-10

The combustible component is prepared by mixing the ingredients for 1 to 2 hours at a temperature below 140°C. The modifier of the exponent n, stabilizer and surface-active agents are incorporated before the ammonium nitrate. The combustion "catalyzer" and carbon black are mixed with the  $\text{NH}_4\text{NO}_3$  and added to the combustible component at a temperature below 110°C (90-105°C). It is cast into molds under a pressure of 140 kg/cm<sup>2</sup>. The combustion temperature is 800-1370°C.



TABLE 9.5. THE COMPOSITION OF SOME ROCKET PROPELLANTS WITH ASPHALT AND WITH THICKENERS

Propellant number	Constituents	%	Burning rate r	
			wet mixing [cm/sec]	dry mixing [cm/sec]
1	Asphalt	14	0.323	-
	Benton-34*	1		
	NH <sub>4</sub> NO <sub>3</sub>	80		
	(NH <sub>4</sub> ) <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	5		
2	Asphalt	14	0.383	0.295
	Benton-34	1		
	NH <sub>4</sub> NO <sub>3</sub> 85.4%	85		
	Prussian blue 4.3%			
	KNO <sub>3</sub> 10.3%			
3	Asphalt	14	0.523	-
	Benton-34	1		
	NH <sub>4</sub> NO <sub>3</sub> 85.4%	80		
	Prussian blue 4.3%			
	KNO <sub>3</sub> 10.3%			
	(NH <sub>4</sub> ) <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	5		
4	Asphalt	14	0.438	-
	Benton-34	1		
	NH <sub>4</sub> NO <sub>3</sub> 91%	85		
	Furnace black 4.5%			
	KNO <sub>3</sub> 4.5%			
5	Asphalt	14	0.477	-
	Benton-34	1		
	NH <sub>4</sub> NO <sub>3</sub> 91%	80		
	Furnace black 4.5%			
	KNO <sub>3</sub> 4.5%			
	(NH <sub>4</sub> ) <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	5		

\*The product of the reaction of bentonite with dimethyl-diethyl ammonium chloride.

TABLE 9.5. (continued)

Propellant number	Constituents	%	Burning rate r	
			wet mixing [cm/sec]	dry mixing [cm/sec]
6	Asphalt	14	0.256	0.206
	Benton-34	1		
	NH <sub>4</sub> NO <sub>3</sub> 95%	85		
	Prussian blue 5%			
7	Asphalt	14	0.206	-
	Benton-34	1		
	NH <sub>4</sub> NO <sub>3</sub> 90%	85		
	KNO <sub>3</sub> 10%			

Example<sup>2</sup>

An equivalent amount (here, 5 parts) of the 2.1:3 mixture of 2,4-dinitro toluene and 2,4-dinitro-diphenyl ether is added at 130-140°C to 2 parts of the styrene-acrylonitrile copolymer (29 mole percent of acrylonitrile) and 3 parts of asphalt (softening point, 102-113°C). This is mixed at 110°C for 2 hours.

82 parts of the mixture: 79 parts of NH<sub>4</sub>NO<sub>3</sub> with 3 parts of insoluble Prussian blue, are added to 18 parts of the combustible component and mixed for 1 hour at 100-110°C.

The finished propellant has the following composition:

	%
NH <sub>4</sub> NO <sub>3</sub>	79
asphalt	5.4
styrene-acrylonitrile copolymer	3.6
2,4-dinitro toluene	3.7
2,4-dinitro phenyl ether	5.3
Prussian blue	3.0

<sup>2</sup>See page 345

This propellant is cast at 100°C under a pressure of 239 kg/cm<sup>2</sup>. It tolerates a temperature of 77°C for 30 days and the cyclic test from -60 to +77°C. The burning rate is 0.356 cm/sec. Other examples of propellants of this type are given in Table 9.6 [65].

TABLE 9.6. THE COMPOSITION OF SOME ROCKET PROPELLANTS WITH ASPHALT IMPROVED BY THE STYRENE-ACRYLONITRILE COPOLYMER

Constituents (in %)	Propellant number				
	2	3	4	5	6
Asphalt	3	4.9	4.9	5.7	1.2
The styrene-acrylonitrile copolymer	2	3.2	3.2	3.8	9.2
2,4-dinitro-diphenyl ether	3	4.8	4.8	5.7	3.4
2,4-dinitro toluene	2	3.3	3.3	3.8	-
Triethyl citrate	-	-	-	-	4.6
Di(2,4-dinitro-phenyl) triethylene glycol ether	-	-	-	-	4.6
Prussian blue	3	-	3	-	-
Carbon black	-	-	-	3	3
Aniline black	-	3.8	1.8	-	-
Sorbitol oleate	0.1	-	-	-	-
NH <sub>4</sub> NO <sub>3</sub>	86.9	80.0	79.0	78.0	74.0
Burning rate r [cm/sec]	0.305	0.254	0.432	0.140	0.109

#### Propellants with asphalt and with polyesters

In order to prevent the cracking of asphalt propellants, the binder can be improved with polyesters. Sebacic acid esters and polyhydroxy alcohol esters have proved to be the most advantageous. They are added to the asphalt, preferably in the ratio of 3:4. The polyester is usually modified with castor oil, which prevents an excessive increase in the length of the polycondensate particles. The undesirable fluidity of the propellant at elevated temperatures is eliminated by the addition of certain waxes with a melting point higher by at least 70°C than the

temperatures to which the propellant is subjected. Because some waxes have a tendency to harden at low temperatures, which in turn can lead to cracking of the propellant, the addition of a plasticizer is imperative.

Generally, the composition of such propellants is as follows:

	%
asphalt	8 --12
glycerin sebacate modified with castor oil	7 --11
dibutyl sebacate	2 ÷ 3.5
cetyl-acetamide (wax)	2.5 ÷ 4
$\text{NH}_4\text{ClO}_4$	75

The wax is incorporated into the molten asphalt and then the mixture of polyester with oil is added. It is successively mixed with the plasticizer and then with the oxidizer; the mixing temperature is 127°C. The following is one of the propellants of this type [92,106]:

	%
asphalt <sup>3</sup>	10.5
glycerin sebacate modified with castor oil	8.0
cetyl-acetamide	3.0
dibutyl sebacate	3.5
$\text{NH}_4\text{ClO}_4$	75.0

The burning rate at 70 kg/cm<sup>2</sup> is 1.26 cm/sec.

#### 9.4. Propellants with Ammonium Nitrate and Amines

The ammonium nitrate mixture can be used to make up almost any type of propellant, depending on the methylamine content in it. With a methylamine content of about 2%, the ammonium nitrate mixtures serve as explosives; from 2 to 6%, as solid rocket propellants; from 6 to 15%, they are muds and can be used as liquid single-constituent propellants; from 15 to 40%, they are liquid solutions and are used for liquid, two-component propellant engines.

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<sup>3</sup>See page 345

It is a very simple matter to prepare the above propellants. The ammonium nitrate is permeated with liquid methylamine. The resultant solution is evaporated down to a 2-6% methylamine content to obtain the solid propellant.

Some explosive mixtures and propellants with ammonium nitrate and methylamine are given in Table 9.7 [83,84].

TABLE 9.7. THE COMPOSITION OF SOME EXPLOSIVE MIXTURES AND ROCKET PROPELLANTS WITH AMMONIUM NITRATE AND METHYLAMINE

Propellant number	Additives (in %)	Methylamine [%]	NH <sub>4</sub> NO <sub>3</sub> [%]
1	high-boiling petroleum fraction 6	2	92
2	coal dust 7	3	90
3	grain flour 7	2	91
4	wood flour 8	2	90
5	carbon black 7	3	90
6	ammonia 6	2	92
7	- -	2	98
8	- -	6	94
9	- -	25	75

#### 9.5. Propellants with Dimethyl Sulfoxide

These propellants are based on low-melting adducts, which were discussed in section 6.1.13. High-energy substances, such as hexogen, penthrite or nitroguanidine, and oxidizers of the nitrate and perchlorate groups can be added to the above adducts. Pulverized metals (aluminum, magnesium) are incorporated in order to increase the combustion temperature.

##### Propellant

78 g of (CH<sub>3</sub>)<sub>2</sub>SO and 18 g of H<sub>2</sub>O are mixed at 80°C and 123 g of anhydrous NaClO<sub>4</sub> and 5 g of aerosol are added. The solution that results is poured over 10 g of cellulose batting in a mold. The finished propellant has a good mechanical



strength and the burning rate is 0.3-0.4 mm/sec [86].

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This review of solid rocket propellants permits the assumption that 2 oxidizers predominate in the propellants in current use: ammonium nitrate and ammonium perchlorate. A great deal of research has been carried out to eliminate the disadvantages of ammonium nitrate because this oxidizer is unusually inexpensive as compared with others (it is about 10 times cheaper than  $\text{NH}_4\text{ClO}_4$ ).

The economic factor is also often decisive in the choice of combustible components. Hence, the expanded research on propellants with pitches, asphalts, tars, frequently improved with synthetic rubbers (particularly, the copolymer 1,3-butadiene -- 2-methyl-5-vinyl pyridine). It is apparent that there is a great future for the propellants consisting of solutions of ammonium nitrate in amines, because of their cheapness, simplicity of production and high chemical stability.

Additives of light metals, particularly, boron, aluminum and magnesium, are more and more frequently used in propellants for special purposes, when it is necessary to obtain a large specific impulse. In connection with this, research has been conducted on obtaining the appropriate particle shape of the pulverized metals.

Investigations have also been (and are being) carried out on high-energy binders (a high calorific value of the binder must be here reconciled insofar as is possible with a high chemical stability) for the purpose of increasing the specific impulse.

New oxidizers, particularly of the organic type, with a high active oxygen content in the molecule and also having high chemical stability, are continually being sought.

#### Footnotes

1. to p. 328. Propellant composition in parts by weight.
2. to p. 340. The prope-lant compositin is given in parts by weight.
3. to p. 342. Asphalt with a softening point of 83-104°C and a penetration of 7-9 mm/5 sec/100 g at 77°C.

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